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INTERNATIONAL SYMPOSIUM

PROCEEDINGS

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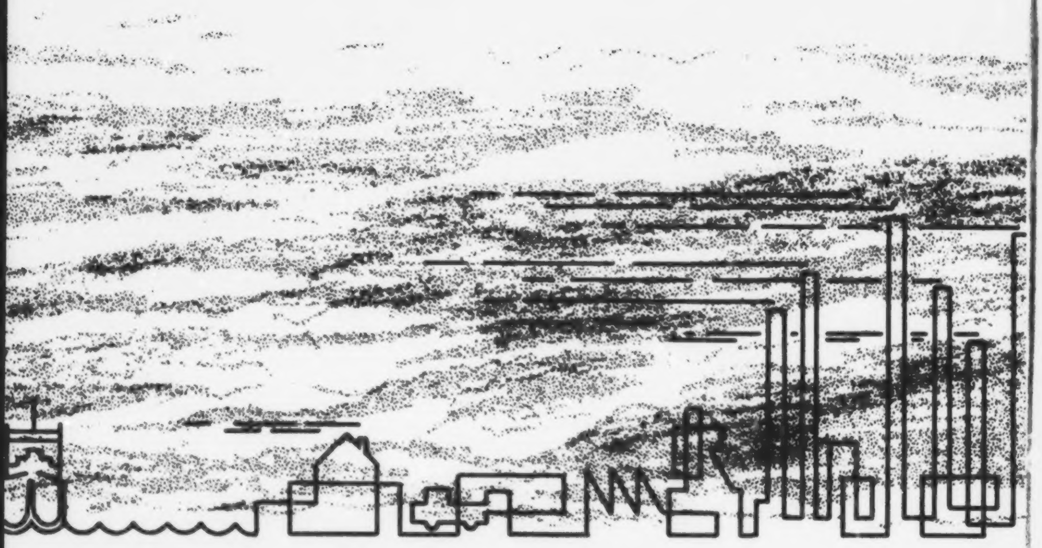
Volume III



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16. ABSTRACT

This publication (in four volumes) contains the full proceedings of this international symposium. It is printed in the original language (Dutch, English, French, German, and Italian) of the individual reports or communications presented, with an English translation of the abstract of each report. The purpose of the meeting was to evaluate the methodologies and techniques available for establishing exposure-effects relationships for environmental pollutants with the goal of encouraging development of sound bases for the establishment of various approaches to protect the public health. These proceedings are made up of more than 250 scientific papers under the broad headings of: The scientific data base required to protect human health, experimental investigations, human effects studies, animal studies, metabolism, interactions, indicators of exposure, population studies, toxicological studies, exposure monitoring, monitoring needs, experimental models, tissue measurements, and environmental measurements. Discussions following papers or groups of papers are also printed. An objective of the symposium was to encourage compatible methodology and data on scientific findings to help ensure that future data will be more directly applicable to the assessment of environmental health effects.

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VORSLAG
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(Continued)

Vorsitzender - Chairman - Président - Presidente - Voorzitter

L. ROSIVAL (C.S.S.R.)

EVALUATION EN MICROSCOPIE OPTIQUE DU DEGRE DE L'EMPOUSSIERAGE PULMONAIRE ASBESTOSIQUE PAR MICROFILTRATION DE L'EXPECTORATION ET DU SUC GASTRIQUE

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RESUME

L'identification et le dénombrement des corps ferrugineux (asbestosiques) et des fibres nues (d'asbeste) ont été réalisés par microfiltration de l'expectoration et du suc gastrique. Trois groupes de sujets ont été étudiés: groupe I, sujets exposés à un fort empoussiérage asbestosique; groupe II, sujets ayant travaillé à la transformation de produits à base d'asbeste et groupe III, sujets exposés à un empoussiérage de type industriel comportant plus ou moins de l'asbeste.

La numération des corps ferrugineux a révélé qu'il existait une corrélation étroite entre le nombre de corps ferrugineux trouvés dans l'expectoration et le nombre de ces mêmes corps trouvés dans le poumon. Il semble qu'au-dessus de la concentration intraparenchymateuse de 1000 corps ferrugineux par cm^3 *de poumon, on retrouve des corps ferrugineux dans l'expectoration, tandis que dans le suc gastrique, le reflet de l'empoussiérage pulmonaire asbestosique n'est mis en évidence qu'à un seuil plus haut d'environ 10 000 corps ferrugineux par* cm^3 *de poumon. La recherche de corps ferrugineux dans l'expectoration apparait donc comme la méthode la plus sensible pour apprécier le niveau de l'empoussiérage pulmonaire par des particules fibreuses.*

L'analyse de l'évolution dans le temps de l'élimination respective des corps ferrugineux et des fibres nues après la cessation de l'exposition professionnelle a permis une étude dynamique de l'épuration à long terme des particules fibreuses: les sujets éliminent d'abord les fibres nues les plus courtes, puis après des années d'évolution, le pourcentage de corps ferrugineux augmente pour atteindre un taux de 80%, 10 ans après la cessation de l'exposition.

ABSTRACT

Ferruginous (asbestos) bodies and naked asbestos fibres were identified and counted by microfiltration of the sputum and gastric secretions. Three groups of subjects were studied: Group I, subjects heavily exposed to asbestos dust: Group II, subjects who had been occupied in the manufacture of asbestos-based products; and Group III, subjects exposed to industrial-type dust containing greater or lesser amounts of asbestos.

Counting of the ferruginous bodies showed a close correlation between the number of these bodies in the sputum and the number found in the lung. It appears that if the concentration of ferruginous bodies within the parenchyma exceeds 1000 per cm^3 *of lung, these same bodies are found in the sputum, but that they are found in the gastric secretions only when the concentration in the lung exceeds the much higher threshold concentration of 10,000 ferruginous bodies per* cm^3 *of lung. Thus, determination of ferruginous bodies in the sputum appears to be the most sensitive method for assessing the level of fibrous dust particles in the lungs.*

A comparative analysis of the elimination of ferruginous bodies and naked fibres in the course of time after occupational exposure had ceased permitted a dynamic study of the long-term clearance of fibrous particles. The subjects first eliminate the shortest naked fibres. Then, after the condition has taken its course for some years, the percentage of ferruginous bodies increases, rising to 80% ten years after the end of exposure.

1. INTRODUCTION

Dans des publications précédentes (1,2), nous avons montré que le dénombrement des corps ferrugineux (CF) après microfiltration de l'expectoration constituait une méthode d'investigation clinique très intéressante, permettant d'évaluer, du vivant du malade, et sans avoir recours à la biopsie pulmonaire, la concentration intra-pulmonaire en CF.

Le présent travail a pour but d'établir des données de référence concernant les relations qui existent entre le nombre de CF dans l'expectoration ou dans le produit de tubage gastrique et la concentration intra-pulmonaire, compte tenu de l'importance de l'exposition au risque asbestosique et de l'élimination des fibres après la cessation de l'exposition.

2. MATERIEL ET METHODES

L'étude a porté sur 193 sujets.

L'interrogatoire professionnel a permis d'isoler 56 sujets témoins non exposés à l'asbeste et 137 sujets dont on pouvait supposer une exposition au risque asbestosique au cours de leur vie professionnelle. Le classement des sujets en 3 groupes, en fonction du travail qu'ils exécutaient, a permis d'obtenir une évaluation grossière de l'intensité de leur exposition :

groupe I : 21 cas, âge moyen : 52 ans. "Manipulation de l'asbeste à l'état brut" (broyage, filage, tissage, projection, manutention, etc...) ;

groupe II : 47 cas, âge moyen : 53 ans. "Transformation de produits à base d'amiante" (isolation, chauffage, réparation freins d'automobiles, etc...) ;

groupe III : 69 ans ; âge moyen : 56 ans. "Exposition à un empoussiérage industriel comportant plus ou moins de l'amiante".

Si chez tous les sujets des 3 groupes précédents ont été précisés : nature et durée de la profession et délai depuis la cessation de l'exposition asbestosique. Par contre, la densité de l'empoussiérage et la nature des fibres inhalées n'ont pu être obtenues qu'approximativement dans cette étude rétrospective.

Le dénombrement des fibres d'asbeste a été réalisé après digestion chimique par l'hyochlorite de sodium et microfiltration sur 3 types de prélèvements selon une méthode précédemment décrite (2) : expectoration matinale chez tous les sujets (193 sujets), liquide gastrique prélevé à jeun avant le lever (37 sujets) et parenchyme pulmonaire après fixation formolée en insufflation (52 sujets). Les fibres gainées ou corps ferrugineux (CF) et les fibres nues ont été comptées au microscope optique en contraste de phase (x 400). Le nombre de particules fibreuses a été exprimé : pour l'expectoration et le produit de tubage gastrique : nombre total par prélèvement ; pour le poumon : nombre de CF par cm3 de parenchyme pulmonaire fixé.

3. RESULTATS

1) Relation entre le nombre de corps ferrugineux rencontrés dans l'expectoration ou le liquide de tubage gastrique et le type d'exposition professionnelle.

1°) Epuration des CF dans l'expectoration :

Chez les 56 sujets témoins non exposés professionnellement à l'asbeste, il n'y avait pas de CF dans l'expectoration.

Chez les 137 sujets pour lesquels il existait la notion d'une possible exposition professionnelle à l'asbeste, la fréquence des cas avec expectoration positive était respectivement pour les groupes I, II et III de 95 %, 60% et 25 %. Cette relation apparait encore plus nettement lorsqu'on tient compte du nombre de CF par expectoration : le nombre moyen de CF trouvés était de 100 pour les sujets du groupe I, 10 pour les sujets du groupe II, 1 pour les sujets du groupe III (Fig. 1).

2°) Résultats comparés de l'épuration des corps ferrugineux dans l'expectoration et dans le produit de tubage gastrique (T.G.), :

Chez 37 sujets, ont été comparés les résultats de la recherche des CF dans l'expectoration et dans le T.G. Chez 26 de ces sujets, la recherche était négative dans les deux produits. Pour les 11 patients avec CF dans l'expectoration, le nombre de CF trouvés dans le T.G. était toujours nettement inférieur à celui trouvé dans l'expectoration.

Il apparait donc que la recherche des CF dans l'expectoration est plus sensible que dans le T.G. pour apprécier le niveau d'élimination des particules fibreuses. L'étude des sécrétions gastriques étant à réserver aux sujets sans expectoration.

2) Corrélation avec l'empoussiérage pulmonaire

Dans 52 cas étudiés, le nombre de CF/cm3 de parenchyme pulmonaire (3) a été comparé à celui trouvé dans l'expectoration (Fig. 2)

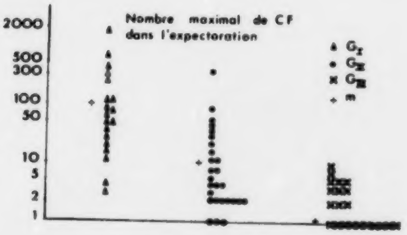

Figure 1

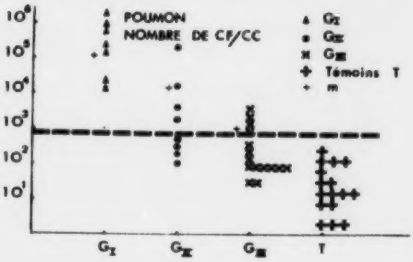

Figure 2

Figure 1 : Corrélation entre le nombre de CF rencontrés dans l'expectoration et le type d'exposition professionnelle.
Pour chaque cas, ce nombre est représenté en utilisant une échelle logarithmique (+ indique la moyenne du nombre de CF dans chaque groupe).

Figure 2 : Corrélation entre le nombre de CF rencontrés par cm3 de parenchyme pulmonaire et le type d'exposition professionnelle.
Pour chaque cas, ce nombre est représenté en utilisant une échelle logarithmique (+ indique la moyenne du nombre de CF dans chaque groupe).

Chez les 20 témoins de cette série, sans exposition professionnelle et avec expectoration négative, le nombre de CF trouvé par cm3 de parenchyme pulmonaire variait entre 2 et 150 (moyenne - 50).

Chez les 32 sujets avec risque asbestosique certain ou probable, les résultats variaient en fonction de l'intensité du risque.

Ainsi, pour le groupe I, la moyenne de 100 CF trouvés dans l'expectoration correspondaient à une concentration pulmonaire moyenne d'environ 100 000 CF/cm3 ; pour le groupe II, la moyenne de 10 CF de l'expectoration correspondait à une concentration pulmonaire moyenne d'environ 10 000 CF/cm3 ; pour le groupe III, la moyenne de 1 CF dans l'expectoration correspondait à une concentration pulmonaire d'environ 1000 CF/cm3.

D'une manière générale, il semble donc qu'il existe une relation entre le nombre de CF trouvé dans l'expectoration et la concentration en CF. Les résultats sont exprimés sur la Fig. 3, qui montre que = 1000 CF/cm3 de parenchyme pulmonaire représente une valeur seuil (les résultats sont représentés suivant une double échelle logarithmique).

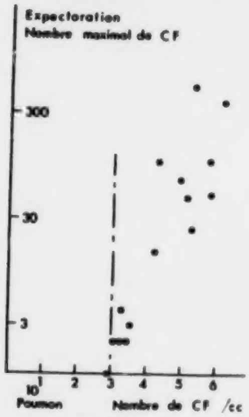

Figure 3

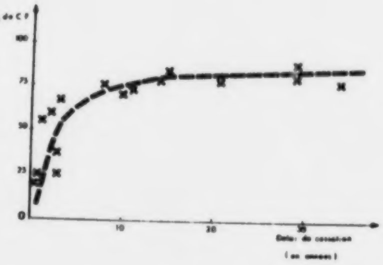

Figure 4

Figure 3 : Corrélation entre le nombre de CF dans l'expectoration et le nombre de CF rencontrés dans les prélèvements de parenchyme pulmonaire ; les résultats sont représentés suivant une double échelle logarithmique.

Figure 4 : Variation du rapport des fibres gainées ou CF par rapport au nombre total des CF + fibres nues en fonction du délai de cessation.du risque asbestosique.

3) Etude de l'épuration des particules fibreuses à long terme

Dans 15 observations où fibres nues et enrobées ont été dénombrées à la fois dans l'expectoration et dans le parenchyme pulmonaire, le pourcentage des fibres enrobées (CF) et des fibres nues variait suivant le délai de cessation de l'exposition. Ainsi, dans les années suivant la cessation de l'exposition, ce sont les fibres nues, surtout courtes (4) qui dominent dans l'expectoration. Par la suite, on constate que le pourcentage de CF, correspondant à l'enrobement de fibres longues augmente rapidement avec le temps pendant une période de 10 ans environ, pour ensuite se stabiliser à environ 80 % et rester à ce niveau à peu près constant.

Il est cependant intéressant d'observer que sur les cas étudiés, nous n'avons identifié le chrysotile qu'une seule fois dans les prélèvements de parenchyme pulmonaire. Ces résultats concordent avec ceux observés par d'autres auteurs (5,6,7) qui constatent une prédominance des variétés d'asbestes amphiboles dans le tissu pulmonaire. Le problème de la pénétration alvéolaire des fibres de chrysotile et de la cinétique de leur épuration reste donc non résolu.

Bien que préliminaires, ces résultats indiquent les modalités de l'épuration pulmonaire à long terme des particules fibreuses chez l'homme. Jusqu'à ce jour, les études analytiques réalisées, n'ont pu l'être que chez l'animal (8,9,10). Or la connaissance des modes d'épuration chez l'homme apparait pourtant fondamentale (11), puisque de la durée de rétention intra-pulmonaire des fibres d'asbeste dépend un effet pathogène plus ou moins marqué (5), notamment en ce qui concerne l'action cancérigène.

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DISCUSSION

COOPER (U.S.A.)

Avez-vous eu l'occasion d'utiliser cette technique pour étudier le cas d'ouvriers nouvellement embauchés afin de déterminer si cette technique pourrait constituer un système de détection et de surveillance de la surexposition? Il est bien connu que des ouvriers subissant une forte dose d'exposition peuvent continuer à expectorer des corps ferrugineux encore pendant plusieurs années après la cessation de l'exposition, mais cette méthode pourrait être appliquée aux nouveaux ouvriers, au moins pour la recherche des amphiboles.

BIGNON (France)

Jusqu'à présent, nous n'avons pas utilisé cette technique pour la surveillance d'ouvriers nouvellement embauchés, mais nous sommes persuadés que l'examen de l'expectoration représente un test très sensible de surveillance de tels sujets. On pourrait par exemple proposer d'interrompre l'exposition dès qu'apparaissent des corps ferrugineux dans l'expectoration.

DUPUIS (France)

Pensez-vous que l'utilisation du microscope optique permet d'identifier les fibres de petites dimensions qui sont vraisemblablement les seuls susceptibles d'induire des mésothéliomes?

BIGNON (France)

Malgré l'utilisation de techniques microscopiques élaborées (1), comme l'observation en contraste de phase, ou la technique des liqueurs d'indice, il est évident que les fibres de taille inférieure à 3 microns peuvent échapper à l'examen en microscopie optique.

Le problème se pose tout particulièrement pour la détermination des fibrilles élémentaires de chrysotile dont le diamètre de 300 Å les rend pratiquement inaccessible à la microscopie optique, les fibres que l'on peut observer étant alors des associations de fibrilles élémentaires. Il faut utiliser le microscope électronique pour résoudre ces fibrilles.

Néanmoins, la microscopie optique constitue une méthode excellente pour apprécier le degré d'empoussiérage d'une région tissulaire, ceci grâce aux méthodes de préparation qui sont simples et très reproductibles. Il convient ensuite d'utiliser la microscopie électronique pour établir une granulométrie des particules et réaliser une identification plus précise par microdiffraction.

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GIBBS (Canada)

La méthode que vous avez utilisée pour l'identification du type de fibre présent dans les poumons des ouvriers vous permet-elle de déterminer de quel type d'amphibole il s'agissait?

BIGNON (France)

Pour ce travail, l'identification des fibres a uniquement été réalisée par microdiffraction électronique. Si par cette méthode, il est très facile de distinguer amphibole et chrysotile, la distinction entre les différents types d'amphibole est, à notre sens, impossible d'après le seul examen du cliché de microdiffraction.

Pour identifier précisément le type d'amphiboles, il faut utiliser plusieurs microméthodes physiques:

- Optique cristalline: par cette méthode, on mesure particulièrement l'indice de réfraction et le signe de l'allongement.

- Microanalyse chimique élémentaire: les fibres d'amphiboles peuvent avoir une taille suffisante pour qu'avec le MEB équipé d'un système dispersif, on accède à la chimie élémentaire d'une façon semi-quantitative.

Mais ces méthodes sont longues et coûteuses et n'ont pas été utilisées dans cette enquête.

ETUDE QUANTITATIVE EN MICROSCOPIE OPTIQUE ELECTRONIQUE DE L'EMPOUSSIERAGE PULMONAIRE ET PLEURAL CHEZ VINGT SUJETS

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RESUME

De nombreux travaux menés tant en France qu'à l'Etranger, il ressort que la plupart des adultes vivant en milieu urbain, ont des corps asbestosiques ou ferrugineux dans leur parenchyme pulmonaire: nous avons fait la même constation chez les sujets vivant dans l'agglomération Havraise.

Or, en matière d'asbestose professionnelle, la plupart des auteurs attribuent un pouvoir pathogène aux fibres d'amiante restées nues, bien plus qu'aux corps asbestosiques.

Dans ces conditions, il nous a paru intéressant de comparer en microscopie optique et électronique la teneur en fibres d'amiante du tissu pulmonaire et pleural de sujets soumis les uns à une exposition massive, les autres à un risque faible, bref ou apparamment nul.

ABSTRACT

Numerous studies in France and in other countries have shown that most adults living in an urban environment have asbestos or ferruginous bodies in the pulmonary parenchyma. We have found the same in subjects living in the area of Le Havre.

With regard to occupational asbestosis, most authors consider that asbestos fibres which have remained naked are much more pathogenic than asbestos bodies.

In these circumstances, we thought it would be of interest to compare by optical and electron microscopy the asbestos fibre content of the lung and pleural tissue of some subjects who had undergone massive exposure and others who had been exposed to slight or short-term risk, or to no apparent risk.

Matériel et Méthodes

Le présent travail porte sur 20 malades:

- 12 ont été soumis à un empoussiérage professionnel massif par l'amiante
- 8 à un risque faible, bref ou apparamment nul.

Nous comparons les résultats à ceux d'une étude antérieure en microscopie optique déja publiée portant sur:

- 52 sujets non sélectionnés
- 12 porteurs de mésothéliomes
- 11 asbestoses majeures.

Dans chacune de nos 20 observations, nous avons détruit 4 gr de tissu pulmonaire ou pleural formolé par digestion alcaline. Le produit obtenu est lavé et ramené par centrifugation à un culot de 1 cm^3. Une goutte de 20 ml est prélevée pour étude au microscope électronique Sopelem 75, soit directement (empoussiérage faible) soit après une nouvelle dilution (empoussiérage élevé) Le coulot initial est filtré sur une membrane Millipore à 3 microns qui permet après clarification, la numération au microscope optique des corps asbestosiques.

Par cette méthode il est possible de comparer la teneur en corps asbestosiques d'une part, et en micro-fibres d'amiante de dimension infra-microscopique d'autre part, d'une masse standard de tissu fixé.

En raison de l'existence de plusieurs temps de centrifugation décantation, il est possible que nous sous-estimions la teneur en micro-fibres, par contre une surévaluation nous parait peu probable.

Résultats

Nous rappellerons brièvement les données de notre étude quantitative préalable où:

96% de nos sujets ont des corps asbestosiques dans leur parenchyme pulmonaire.

Nous avons ventilé nos résultats en quatre groupes selon le nombre de corps asbestosiques (C.A.) contenus dans 4 gr de poumon.

- 1 moins de 10^2 C.A.
- 2 de 10^2 à 10^3 C.A.
- 3 de 10^3 à 10^4 C.A.
- 4 plus de 10^4 C.A.

Tous les sujets non sélectionnés figurent dans les groupes 1 et 2. Les asbestoses professionnelles avérées se situent dans le groupe 4. Les observations de mésothéliome font transition et se classent dans le groupe 3.

Ces données sont comparables à celles de la littérature.

L'étude couplée en microscopie électronique nous a permis dans un premier temps de classer nos observations selon ces groupes:

En microscopie optique:

- 13 observations sont du groupe 4
- 3 " sont du groupe 3
- 4 " sont du groupe 1 et 2.

En microscopie électronique:

Nous observons des fibres nues dans tous nos échantillons de parenchyme pulmonaire ou de plaque pleurale.

Pour les empoussiérages de type 4 en microscopie optique la concentration pulmonaire en fibres infra-microscopiques atteint des chiffres de l'ordre de 10^6 à 10^7.

Nous reproduisons ici un tableau portant sur 6 de ces observations où la répartition des fibres est assez homogène sur plusieurs échantillons pour autoriser une évaluation quantitative rapportée au volume initial dissous.

Observations n°s	C.A. Optique	Fibres nues électronique
30. 606	11. 10^4	12. 10^6
A. 481	6,9.10^5	3. 10^7
A. 691	1,5.10^4	3. 10^5
A. 1384 b.	4,7.10^5	1,4.10^7
A. 384	1,1.10^5	1,6.10^7
A. 1154	2,2.10^5	3,1.10^7

Pour les observations de type 1 à 2 les concentrations en micro-fibres sont beaucoup plus faibles. L'on observe parfois moins de 10 micro-fibres pour une grille entière.

Dans les limites de notre méthode, le nombre des microfibrilles dépasse donc exceptionnellement des chiffres de l'ordre de 10^3. Bien que nous raisonnions sur un petit nombre d'observations, il semble donc exister un hiatus quantitatif considérable entre les empoussiérages pulmonaires de type professionnel et ceux de rencontre tant en microscopie optique qu'électronique surtout.

Dans laplèvre ou plutôt dans les plaques pleurales les concentrations en corps absestosiques visibles en microscopie optique sont très faibles dépassant rarement 100 (10^2).

En microscopie électronique l'on retrouve constamment des microfibres d'amiante: elles sont en général plus petites que dans le poumon homologue.

Certaines observations nous montrent d'importants phénomènes de concentration locale pleurale pour des empoussiérages pulmonaires faibles.

Ex : 75 C.A. dans 4 gr de tissu pleural hyalin
69 C.A. dans 4 gr tissu pulmonaire homologue.

Dans ce travail nous ne retrouvons pas au niveau de la plèvre l'écart qui existe dans le poumon entre les empoussiérages de type professionnel et de type occasionnel.

Discussion

Bien que notre enquête repose sur un nombre limité d'observations, il apparaît cependant que les empoussiérages pulmonaires massifs des asbestoses professionnelles correspondent à des concentrations parenchymateuses en fibres d'amiante sans commune mesure avec celles relevant d'expositions de recontre.

Dans le premier cas, tous nos sujets présentaient cliniquement et radiologiquement d'intenses lésions de fibrose pulmonaire. Dans la seconde éventualité nous n'avons noté au maximum que de discrètes lésions de fibrose histologique.

Au niveau de la plévre par contre, si les concentrations tissulaires sont beaucoup plus faibles, l'on ne retrouve pas un tel hiatus sur le plan quantitatif. Cette constatation nous semble devoir être rapprochée de la grande fréquence avec laquelle nous observons des plaques pleurales hyalines calcifiées ou non à l'autopsie de sujets faiblement exposés d'une part et de l'existence de mésothéliomes chez le même type de malades d'autre part.

D'un point de vue qualitatif, comme beaucoup d'auteurs, Heppelston et Ashcroft en particulier, nous avons surtout identifié chez nos sujets des fibres du type amphibole et plus rarement du chrysotile en longues fibres ou écheveaux touffus. Nous n'avons pas eu l'occasion d'observer comme Selikoff et Langer ont pu le faire chez les habitants de New York, de nombreuses micro-fibrilles de chrysotile.

Les enquêtes de risque menées chez nos malades ou dans leur entourage professionnel nous laissent à penser qu'actuellement l'empoussiérage pulmonaire par l'amiante dans l'agglomération havraise relève plutôt d'une exposition professionnelle faible ou occasionnelle, dont la fréquence va d'ailleurs augmentant, que d'un problème de pollution générale. Il est possible que cette situation évolue dans les années à venir.

L'amplification des études quantitatives pour difficiles qu'elles soient nous parait constituer une voie intéressante pour apprécier la signification de ces empoussiérages faibles en les comparant aux asbestoses massives.

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DISCUSSION

BRUCH (République fédérale d'Allemagne)

Avez-vous déterminé le rapport entre les particules d'amiante (PA) et les fibres nues dans le poumon pour les 4 groupes d'expérience? En expérimentation animale (avec P.F. Holt) la formation de PA par détérioration de macrophages alvéolaires combinée à d'autres causes telles que le tabagisme a été arrêtée. Le résultat fut que les lésions pulmonaires étaient d'autant plus graves que l'on dénombrait moins de PA. Il se pourrait donc que, chez des malades (mésothéliome et/ou fibrose) le rapport PA - fibres nues soit abaissé. Nous partons de l'hypothèse que la formation de PA est un mécanisme d'épuration du corps. Une disposition individuelle différente du corps pourrait expliquer que certaines personnes soient atteintes alors qu'elles n'ont subi qu'une exposition relativement peu importante.

FONDIMARE (France)

Nous avons étudié le rapport corps asbestosique/fibres nues chez les sujets très empoussierés seulement. Le nombre des corps asbestosiques augmente en fonction du temps et varie avec le type d'amiante inhalé.

GIBBS (Canada)

Il nous arrive fréquemment d'examiner le parenchyme pulmonaire de sujets atteints de mésothéliome pour identifier le type de fibre présent (par exemple amosite, crocidolite, trémolite, chrysolite, etc.). Etant donné qu'il existe actuellement des méthodes permettant l'analyse microchimique des différentes fibres, avez-vous l'intention d'utiliser ces méthodes pour l'obtention d'une telle information?

FONDIMARE (France)

Nous distinguons par diffraction d'électrons le chrysotile des amphiboles. Nous ne disposons pas actuellement des méthodes de microanalyse.

DETERMINATION OF CADMIUM IN BLOOD USING A 4.0 MM PAPER DISC - GRAPHITE FURNACE TECHNIQUE. APPLICATION TO INDUSTRY

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ABSTRACT

A paper disc flameless AAS method is described for the determination of Cd in blood, enabling difficulties in sample preparation to be minimized. By control of the ashing step, the matrix can be removed without loss of Cd. Problems with the fast signal response during atomization can be met by spectral band width and temperature control. At the 106 picogram level (5.3 μg/100 ml blood) the R.S.D. was 0.06.

Results in three industrial situations are reported. The method should facilitate further investigation of its application to industry using capillary or venous blood.

1. Introduction

The increasing interest in environmental pollutants has focussed recent attention on cadmium (Cd). This metal is widely used in industry, but knowledge regarding its absorption and excretion is incomplete, thus rendering difficult the interpretation of industrial exposure using biological methods. Measured by a polarographic technique, Cd in the urine of the general population is less than 5 µg/l. In the industrially exposed, greater quantities may be found. Urinary excretion of Cd is commonly used as an index of absorption, and the finding of 25 µg/l is considered evidence of undue exposure. This does not, however, reflect the total body burden or the concentration in vulnerable organs, such as the kidney or the lung.

Absorbed Cd is conveyed in the bloodstream, either cell or plasma bound, throughout the body. Correlation between the urine (UCd) and blood cadmium (BCd) is poor and indeed neither measurement is regarded as a good index of absorption by some authorities. Moreover, the UCd does not necessarily reflect recent exposure. Tissue biopsy has been advocated by Ullucci and Hwang (1) in view of the problems of blood and urinary findings.

From the practical viewpoint, however, for the detection of evidence of undue absorption of Cd in industrial workers, a simple test is needed, acceptable to workers and management, which can be related to exposure in order to alert the Industrial Hygienist to advise on control of environment before concentration in the critical organs can occur, resulting, for example, in tubular nephritis with associated proteinuria.

This paper describes recent developments in the use of atomic absorption spectrometry (AAS) for the estimation of BCd which can be readily adopted for the study of venous or capillary specimens collected from workers in the factory.

The tantalum sampling boat achieved a relative detection limit for Cd of 0.2 ng/ml^{-1} using a 0.5 ml sample of blood, but 16 hours were needed for oxidation (Hauser et al (2)). Ediger and Coleman (3) ignited 10 ml of blood in a Delves sampling cup near the flame and obtained results comparable to those using an extraction/graphite furnace technique. There may be loss of Cd using this method of oxidation since the vapour pressure temperature (VPT) of Cd is little higher than that required to burn blood. Other methods using the Delves cup after pre-treatment of the sample have shown that recoveries, reproducibility and sensitivity are satisfactory (Joselow and Bogden (4) and Lieberman (5)). The latter also reported that the method overcame interference effects of different matrices. Ullucci and Hwang (1) favoured solvent extraction of the Cd prior to determination on a tantalum ribbon, but calibrated the blood figures with aqueous standards.

There are few published references to flameless methods. Dolinšek et al (6) determined Cd in blood using the graphite furnace without pretreatment of the sample which was dried, ashed and atomized in situ. This direct approach to analysis of metals has the advantage of minimising problems due to contamination. The graphite furnace technique enables Cd to be determined on capillary or venous samples directly without pretreatment and with adequate sensitivity.

2. Materials and Methods

2.1 Collection of Specimens

Blood Venous or capillary blood samples were used as indicated in the tables and text collected on the lines described by Cernik and Sayers (7). Capillary blood was spotted onto Whatman's No. 4 filter paper.

Urine Casual specimens of urine were collected from workers in the factory. Corrections were not made for specific gravity, which varied widely.

2.2 Apparatus

A Varian Techtron AA5 spectrometer was used with a CR63 graphite furnace workhead. The graphite cups, 4.5 mm in diameter, were supported by two side electrodes with the correct end radius. Other features were as described by Cernik (8) except for the following:

Cadmium lamp current 4mA. Spectral band width 0.33nm. Wavelength 228.8nm.

Workhead Power Controls For ashing, 12 seconds at 300°C (±10). For atomization, 2.0 seconds at 600°C (±10).

2.3 Method

All blood specimens whether venous or capillary examined by AAS were done by the punched disc technique using 4.0 mm discs after previous spotting in the case of venous blood, as described elsewhere (Cernik (8)). Non-atomic absorption that appeared in the Cd position was controlled to 0.01 absorbance by the use of a hydrogen lamp. A non-interfering second peak was ignored (Fig. 1).

Working Standards Cadmium chloride ($CdCl_2$) solution was mixed with blood samples to give a final added concentration of 0.0, 2.0, 4.0, 6.0, 8.0 and 10.0 μg Cd/100 ml blood.

Ashing of Matrix Precise control of the voltage applied over a given

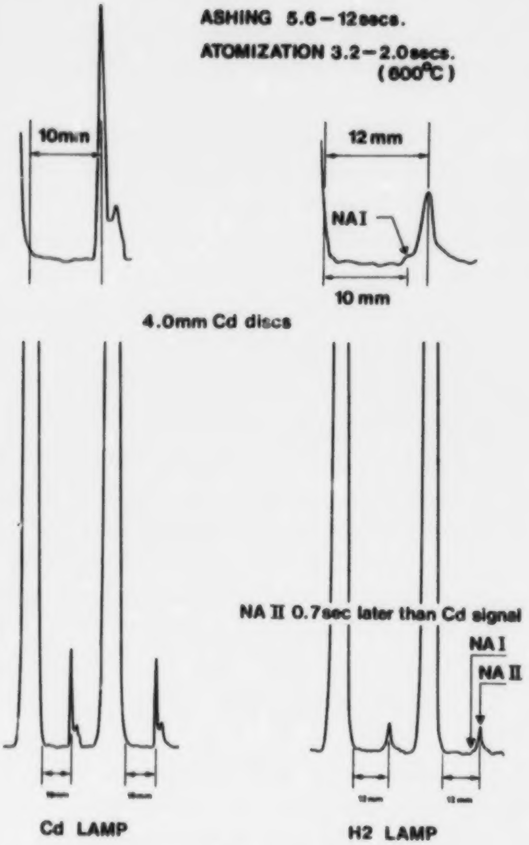

Fig. 1. Non-Atomic signal found in the cadmium position when 4.0 mm blood discs are atomized at 600°C. (NA = non-atomic)

time constant is important for the ashing of the matrix because of the volatility of Cd. Previous work with lead using the same technique had shown that, with the voltage required to achieve 300°C for 12 seconds, complete removal of all the molecular absorption from the matrix resulted. The same ashing system was necessary for Cd because the matrix was identical, but, unlike lead, there was only approximately 100°C difference between the ashing temperature and the VPT of Cd. The possibility that Cd might vapourize at lower temperatures than its VPT was considered, and to check this, discs of blood punched from one sample were ashed at increasing voltage settings, and the Cd content determined (Table I).

TABLE I

LOSS OF CADMIUM BY INCREASING THE TEMPERATURE AT THE MATRIX ASHING STAGE

Ash Control Setting		Temperature $^\circ C \pm 10^\circ$	% Loss Cadmium
5.6	All at 12 seconds.	300	Nil
5.7		340	Nil
5.8		370	6.0
5.9		390	10
6.1		425	45

TABLE II

ATOMIZATION TEMPERATURES AND RESIDUAL CADMIUM (SBW 0.33nm)

Atomize Control Setting (All 2.0 Secs)	Temperature $^\circ C \pm 10^\circ$	Cadmium Peak Height	Residual Cd Peak Height
2.0	450	32	8.0
2.5	490	35	7.0
3.0	515	35	3.0
3.2	600	39	1.0
3.5	625	43	1.0

TABLE III

PRECISION OF REPLICATE ANALYSES USING 4.0 mm DISCS AT THREE DIFFERENT CONCENTRATIONS OF BLOOD CADMIUM

Mean µg Cd/100 ml	Standard Deviation	Relative Standard Deviation
0.8	0.07	0.088
2.0	0.11	0.055
8.2	0.35	0.043

No. of replications at each concentration = 11

TABLE IV

COMPARISON OF MICROMETHOD AND CATHODE RAY POLAROGRAPHY
μg Cd per 100 ml BLOOD

	4.0 mm P.D.		Polarography
	Venous	Capillary	Venous
1.	0.4	0.6	0.5
2.	0.4	0.6	0.9
3.	0.5	1.2	0.8
4.	0.5	1.1	0.8
5.	0.9	1.4	1.6
6.	1.4	1.4	1.0
7.	2.2	1.9	3.0
8.	2.8	5.4	3.5
9.	4.8	5.5	8.1
10.	5.0	4.8	4.9
11.	5.7	5.0	1.9
12.	6.5	7.4	5.4
13.	6.8	7.2	5.5
14.	7.8	7.7	6.0
Mean	3.26	3.66	3.14
S.D.	2.73	2.73	2.45

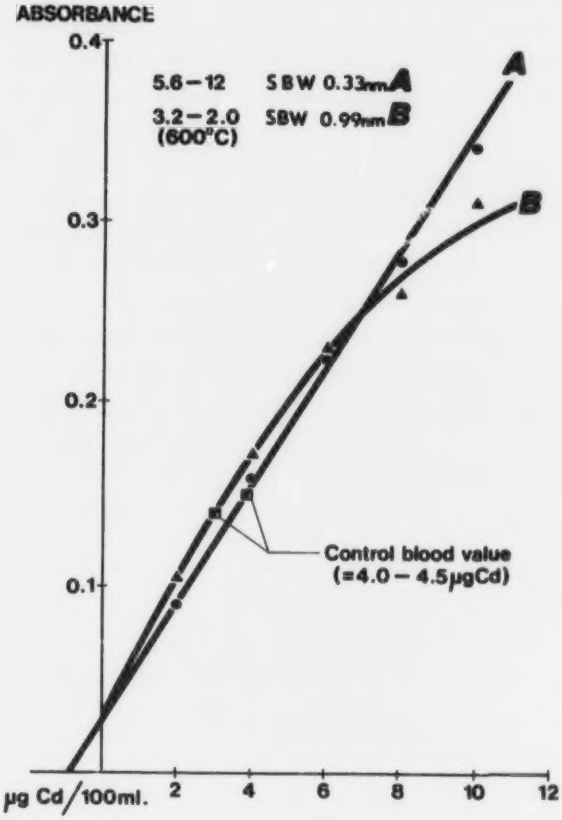

Fig. 2. Effect of spectral band width and volatilization temperature on the linearity of calibration.

Atomization and SBW Effect. Using a relatively high atomization temperature (1200°C), calibration graphs obtained from the range 0-10 g Cd/100 ml blood curved irrespective of SBW (0.33 to 0.99 nm). Reproducibility was also erratic. Reduction of the Volatilization temperature to approximately 600°C produced linear analytical graphs only when the SBW was 0.33 nm. (Fig. 2.) To establish the optomum lowest temperature setting for the best vapourization of the Cd, blood discs from a sample were atomized at increasing temperatures (using SBW of 0.33 nm) and the residual Cd checked (Table II).

3. Results

3.1 Venous and capillary blood specimens and urine samples were collected from workers engaged in two industrial processes using Cd for pigment manufacture and smelting respectively. The first is a dusty process where ingestion is the chief mode of absorption, whereas fume is the principal hazard in the second. Specimens were also collected from workers where there was little Cd risk and from non-exposed controls.

3.2 Precision and Accuracy

Three different naturally occurring Cd concentrations in blood were determined and the results from eleven replications are shown in Table III. To evaluate the punched disc (PD) results, we compared both the capillary and venous samples against results obtained using our standard method of cathode ray polarography in 14 cases (Table IV). The correlation between the venous results done by PD and polarography (POL) was 0.81 and between the capillary results and POL was 0.85. The corresponding correlation

TABLE V

BLOOD CADMIUM IN THE UNEXPOSED
(μg per 100 ml BLOOD)

(Micromethod)

	Venous	Capillary
1.	0.2	0.2
2.	0.2	0.2
3.	0.2	0.2
4.	0.8	0.6 *
5.	0.5	0.5
6.	0.2	0.3
7.	0.2	0.2
8.	0.8	0.6 *
9.	0.3	0.2
10.	0.6	0.6 *

* Smokers

TABLE VI

LEVELS OF BLOOD CADMIUM FOUND

		"Unexposed" Lab.Staff	Naval Dockyard (Silver Brazing)	Pigment Factory (Dust Exposure)	Smelting Factory-1 (Fume Exposure)	Smelting Factory-2 (Fume Exposure)
Number of Comparisons		10	33	14	17	8
Mean	(Venous	0.40	0.37	2.66	4.20	5.20
	(Capillary	0.36	0.51	2.74	5.23	5.61
Standard Deviation	(Venous	0.25	0.19	2.37	2.38	1.94
	(Capillary	0.19	0.34	1.81	3.55	1.89
Range of Samples	(Venous	0.2 - 0.8	0.2 - 0.9	0.5 - 10.3	1.1 - 8.9	2.2 - 7.8
	(Capillary	0.2 - 0.6	0.2 - 1.4	1.1 - 8.5	1.5 -13.3	1.9 - 7.7

between the 14 capillary and venous results was 0.96.

3.3 Normal Values

Ten volunteers with no history of exposure to Cd were bled and capillary and venous specimens examined for Cd. The results are given in Table V. No urines were examined in this series.

TABLE VII

FINDINGS IN COLOUR FACTORY WORKERS

	μg Cd per 100 ml Blood P.D.		μg Cd/litre Urinary Cd (not corrected for SG)
	Venous	Capillary	POL
1.	0.5	1.7	N.D.
2.	1.0	1.1	N.D.
3.	1.5	1.4	N.D.
4.	1.7	2.6	N.D.
5.	1.7	1.3	4.6
6.	1.8	2.6	N.D.
7.	1.8	3.0	<3.0
8.	2.0	2.4	N.D.
9.	2.0	2.4	3.9
10.	2.8	2.8	N.D.
11.	3.0	2.6	N.D.
12.	3.3	2.2	7.2
13.	3.8	3.8	13.8
14.	10.3	8.5	47.0

3.4 Workers engaged in brazing (with no exposure for 5-8 weeks)

33 workers in a Naval dockyard who had been engaged in pipe jointing by silver brazing with Cd-containing alloy were examined. None of these men had been exposed for 5-8 weeks prior to examination. Results of BCd done on venous and capillary specimens are summarised in Table VI. Although the low blood findings confirmed the absence of recent exposure, the urinary results showed quantities ranging from 2-83 µg/l in 9 of the 33 workers. (It was not detectable in the remaining 24.) It is well known that urinary excretion of Cd persists long after exposure to Cd has ceased.

3.5 Workers in a Pigment Factory exposed to Cd Oxide Dust

The corresponding results in 14 workers engaged in pigment manufacture are given in Table VII. Environmental measurements had not been taken recently in this factory. (We also sampled managerial, clerical and laboratory staff whose findings were normal and are excluded from the table.)

3.6 Workers in Two Cd Smelting Factories

Results in 25 workers in two factories exposed to Cd fume are also summarised in Table VI and the actual findings in the second factory are given in Table VIII. Environmental measurements in this factory showed

TABLE VIII

FINDINGS IN SMELTING FACTORY WORKERS

	µg Cd per 100 ml Blood P.D.		µg Cd per litre Urine (Not corrected for SG)
	Venous	Capillary	POL
1.	7.8	7.7	35.0
2.	4.8	5.5	14.8
3.	2.2	1.9	12.6
4.	2.8	5.4	9.7
5.	6.8	7.2	75.0
6.	5.7	5.0	31.0
7.	6.5	7.4	22.0
8.	5.0	4.8	31.0

seven samples out of ten to be above the current TLV (0.1 mg Cd/M^3). (5 workers in the first factory with only intermittent exposure are excluded from Table VI.)

4. Statistical Analysis of Results

4.1 Venous against Capillary BCd

There is good correlation (0.93) between the results of BCd done on venous and capillary specimens (Fig.3). All results are included and the mean of the venous samples was 1.74 µg/100 ml (SD = 2.27) and the mean of the capillary samples was 2.02 µg/100 ml (SD = 2.67). Capillary results tend to be higher in the exposed groups which could be regarded as an advantage in the context for which the technique is recommended in that the method "fails safe".

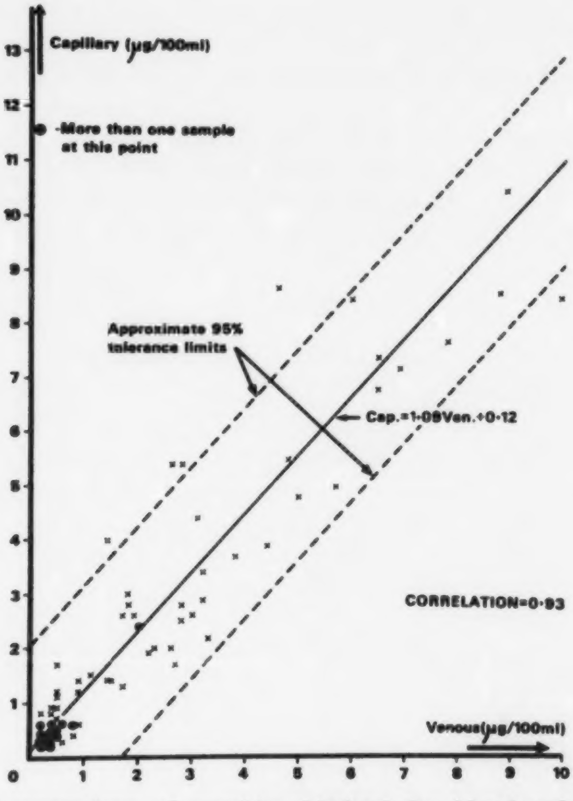

Fig. 3. A comparison of results obtained for blood cadmium using venous and capillary specimens. The regression line is shown and approximate 95% tolerance limits.

4.2 Comparison of Blood and Urinary Cd

Comparisons of BCd and UCd show that if Cd is detected in the urine then the mean BCd of the workers concerned is greater than the corresponding mean in those with no Cd detectable in the urine. There also appears to be an upward trend in the mean BCd as the amount of UCd increases (Table IX). The range of the BCd at the different urinary concentrations was, however, wide.

TABLE IX

COMPARISON OF BLOOD AND URINE CADMIUM

Cd in Urine µg/l	Not Detectable			≤ 5			≥5 ≤10			>10		
Cd in Blood µg/100ml	No.	Mean.	S.D.	No.	Mean.	S.D.	No.	Mean.	S.D.	No.	Mean	S.D.
	47	0.66	0.73	17	2.5	2.4	6	3.23	2.26	22	3.89	3.00

5. Discussion

It is known that concentrations of Cd in the blood do not necessarily reflect the body burden, but it would seem from the results reported here that BCd may well prove a valuable index of the factory hazard (Table VI).

Until recently results of Cd determinations in blood at the levels found in unexposed workers have been conflicting. Elizabeth Willden (9) found approximately 2 µg/100 ml in normal subjects, while earlier reports, for example, Butt et al (10) have quoted much greater quantities. Problems of methodology may well account for these variations. Cd quantities of less than 1 µg/100 ml quoted by Friberg et al (11) for unexposed workers in Sweden, U.S.A. and West Germany are of the same order as reported here.

There is general agreement that despite fluctuations, BCd concentrations in exposed workers are significantly higher than in unexposed controls. Friberg et al (12) and our experience certainly bear this out.

Although the published data (see Friberg et al (13)) suggest that the BCd may not prove a useful index for control of exposure in man, further investigation is clearly needed. The method described here may facilitate this.

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The work presented here has been submitted for publication to the British Journal of Industrial Medicine.

DISCUSSION

KJELLSTRÖM (Sweden)

We have studied in Sweden the cadmium level in blood and urine of three newly employed workers in a Cd-Ni battery factory where the total cadmium level in suspended particulates were about 50 mg/m^3. Blood and urine samples were taken each week during the first two months and then each month during one year. The blood cadmium increased more or less linearly during the first four months of exposure to reach a steady state 3 times, 4 times and 10 times higher then the pre-exposure level.

During the first year no significant change in urinary cadmium occurred. Thus for early cadmium exposure it seems that blood cadmium after some months should be a better indicator of exposure than urine. For long time low-level exposure we believe increased urinary cadmium is more a reflexion of tubular damage then the exposure.

CERNIK (U.K.)

In our experience the blood Cd will rise above unexposed levels if the environmental Cd levels are in excess of the threshold limit values. With oxide dust hazard the absorption tends to be slower but nevertheless demonstrable. Urinary Cd will not be of much value in these circumstances since tissue uptake and stabilization, will interfere with the Cd absorption - excretion mechanism.

PISCATOR (Sweden)

I want to add to Dr. Kjellström's statement that the workers we examined were exposed to cadmium oxide dust. Exposure to high concentrations of cadmium fumes may cause sharper rises in blood levels of cadmium and may even cause increases in urinary excretion of cadmium.

CERNIK (U.K.)

I agree. It tends to be easier to determine Cd fume absorption, because the blood Cd response can be rapid and reach high initial levels, especially if the sample is obtained during or after the work shift. The urinary Cd in these workers will rise significantly and rapidly if the Cd concentration in the air is prolonged.

THE INCIDENCE OF ELEVATED BLOOD LEAD VALUES IN AN ASYMPTOMATIC PEDIATRIC POPULATION RESIDING IN A MAJOR AMERICAN INDUSTRIAL STATE

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ABSTRACT

In the nation's first state-wide investigation and survey for lead poisoning in an asymptomatic population, blood specimens were obtained from more than 7,700 children between 1 and 6 years of age who resided in 20 Illinois cities of intermediate size (10,000 to 150,000).

During the first screening phase 6,151 children were sampled; 1,147 (18.6%) were found to have evidence of undue absorption of lead (greater than or equal to 40 µg/100 ml) while in 51 (0.8%) of the children unequivocal instances of lead poisoning occurred (greater than or equal to 80 µg/100 ml), according to the guidelines of the Surgeon General of the United States of America.

The percentage of children evidencing undue absorption of lead in each city varied from 9.6% to 31.3%, while the main blood lead levels of the samples from the different cities varied from 19.8 µg/100 ml to 32.9 µg/100 ml.

Preliminary analysis of Phase Two Screening has revealed extremely interesting results. The percent of asymptomatic children screened who demonstrated blood lead values in excess of 40 mcg.% ranged from 5.5% in one location to 13.5% in another locale. These figures are lower than the range reported during

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the 1971 campaign (9.6% - 31.3%). Despite the apparent reduction in range values, it is still alarming to note the significant percentage of children, randomly screened, who demonstrated elevated blood lead levels.

Perhaps a more meaningful and certainly a more significant finding which was demonstrated during the second phase was the fact that while the raw numbers of children (and therefore the relative percentage) with blood lead values equal to or greater than 40 mcg.% was somewhat lower in 1972, the mean blood lead values remained remarkably similar between the two years. The Phase One mean blood lead value for all children tested was determined to be 25.5 mcg.%. Preliminary examination of the 1972 data indicates a mean blood lead value of 27.32 mcg.% (corrected to reduce influence of fluctuating sample size).

The findings suggest that pediatric lead intoxication is not confined to urban slums, but does occur with alarming frequency in smaller communities.

BACKGROUND

Early in 1971, the Governor of Illinois instructed the Department of Public Health to initiate a "lead poisoning program". Program officials questioned the relevancy of a single city approach and chose to expand the project to include approximately 14 cities, each with a minimum population base of 10,000 persons. The marked variance in population density in Illinois served as the primary reason for the approach, and cities were selected which included a wide range of population densities. The data obtained from the testing conducted in each city would help to verify or disprove the hypothesis that population density and housing serve as two basic variables directly associated with lead poisoning[7]. A complete analysis of data from the 1971 program and a preliminary analysis of the 1972 date follows.

MATERIALS AND METHODS

Prior to 1971, the City of Chicago had the only lead poisoning detection program in the State of Illinois,8 yet this program provided services only to one-third of the children in the State. The remainder of the State's population is divided nearly evenly between communities of less than 10,000 people (including rural areas) and communities between 10,000 and 150,000 population[9].

A group of potential target cities from the 149 in Illinois with populations between 10,000 and 150,000 was identified. Initial selection of cities was made on the basis of geographic location, racial composition, population density and available medical facilities necessary for medical follow-up.

Table 1 lists the cities that were screened and describes the population of each. Two of the communities have less than the stated minimum of 10,000 population. They are, however, part of a contiguous urban area, Cook County; hence, their population size is a reflection of more political subdivision than of sociological smallness.

Because earlier work has established a definite seasonal variation of blood lead levels and of number of lead posoning cases, with the peak occurrence of both during the summer months [8,10,11] program implementation was scheduled for the summer of 1971.

Several workers have established that lead posoning cases are most common in children 1-3 years of age [11,12].In order to include any older children that might possibly have elevated blood lead levels, the Illinois Department of Public Health Program was focused on children 1 to 6 years of age.

Blood specimens were collected with sterile, 12 cc. disposable syringes fitted with 1" 21 gauge-A bevel disposable needles. Aliquots of blood were transferred into lead-free heparinized vacutainer tubes (for lead and hemoglobin determinations), and into non-heparinized sterile tubes for serological testing.

The 5.0 ml. of heparinized whole blood for the lead determination was hemolyzed in distilled water, chelated with sodium diethyl dithiocarbonate at a pH of 6.5, extracted with methyl-iso-butyl ketone and analyzed with an atomic absorption spectrophotometer, using a single slot

Table 1

POPULATION DATA OF THE 14 COMMUNITIES
IN WHICH
CHILDREN'S BLOOD LEAD VALUES WERE DETERMINED

CITY	DATE OF SCREENING IN 1971	1970 TOTAL POPULATION	CHILDREN AGES 1-6	NUMBER OF CHILDREN SCREENED	% OF CITY'S CHILDREN AGES 1-6 SCREENED
Aurora	7-20,21	74,182	8,817	449	5.09
Springfield	8-3,4	91,753	9,203	670	7.28
Peoria	8-15,16	126,963	13,043	387	2.97
E. St. Louis	8-17,18	69,996	9,187	376	4.09
Decatur	8-23,24	90,397	13,572	793	5.84
Joliet	8-26,27	80,378	8,442	383	4.54
Rock Island	8-30	50,166	5,091	285	5.60
East Moline	8-31	20,832	2,419	298	12.32
Harvey & Phoenix	9-7	38,242	4,612*	226	4.90
E. Chgo. Hghts.	9-8	5,000	1,004*	172	17.13
Chicago Hghts.	9-9	40,900	5,181	537	10.36
Robbins	9-10	9,641	1,520*	103	6.78
Carbondale	9-11,12	22,816	1,512	264	17.46
Rockford	9-20,21,22	147,370	16,531	1,208	7.31
TOTAL		868,636**	100,134	6,151	6.14

* Population data available from the Bureau of the Census varies with the size of the city. Census data for these communities did not include numbers of children by yearly age groupings. Therefore, the numbers with asterisks were calculated from the ratio of under 5 years population to the 1-6 year populations of the cities for which both numbers were available.

** 20.9% of the total population in middle sized Illinois cities and 7.8% of the total Illinois population.

burner and a wave length of 2170 Ao[13] Standarization against controls of 0,20,40,70,100,200 and 300 mcg.% was performed. Pooled samples were run daily along with the program specimens. The standard deviation of the results of these pooled specimens was 3.0 mcg.%[1]. A blood lead value of 40 mcg.% or greater was considered evidence of undue absorption of lead, and a blood lead value of 80 mcg.% or greater was considered an unequivocal care of lead poisoning [12].

RESULTS

In 1971, six thousand one hundred and fifty one children were screened in 14 cities. This figure represents approximately 6.2% of the total children, in the state, between the ages of 1 and 6 years. Over 5% of the children in the "at risk" age group (1-6 years) were tested in 10 of the 14 communities, and over 10% of children in the "at-risk" age group were screened in the remaining four. A frequency distribution analysis of blood lead reported between 0 mcg.% and 65+ mcg.% revealed marked digital preference at values ending in the integers zero and five.

Table 2 shows the mean blood lead levels ranged from a low of 19.8 mcg.% to a high of 32.9% with the mean blood lead level determined to be 25.5 mcg.% The percentage of children with blood lead values 40 mcg.% ranged from 9.6% to 31.3%. For all cities the number and percent of children with elevated blood lead levels (40 mcg.% or greater) were found to be 1,147 and 18.6%. It is interesting to report that more children (44.5%) had blood lead values between 20 and 39 mcg.% than between 1 and 19 mcg.% (36.9%). Subsequent grouping of 40-59 mcg.%, 60-79 mcg.% etc. showed a decline in the percentage of children tested found to have those blood lead values (Table 3). The mean of the mean blood lead values was calculated in order to reduce the influence of the size of the samples in the different communities. This mean of the mean was 26.0 mcg.%. A similar calculation for the percentage of children 40 mcg.% and over 80 mcg.% showed averages of 19.2% and 0.9% respectively of the children tested had blood lead values above those levels[1].Evaluation and assess-

Table 2

PERCENT OF CHILDREN TESTED HAVING BLOOD LEAD VALUES IN THE FOLLOWING 20 MCG.% RANGES AND THE MEAN BLOOD LEAD VALUE IN EACH COMMUNITY

CITY	0-19 Mcg.%	20-39 Mcg.%	40-59 Mcg.%	60-79 Mcg.%	80+ Mcg.%	Mean Blood Lead Value Mcg.%
Aurora	37.9%	37.9%	16.9%	3.8%	3.6%	28.2%
Springfield	21.5	48.4	23.0	6.1	1.0	31.5
Peoria	22.0	46.8	22.2	7.5	1.6	32.9
E. St. Louis	30.1	45.2	19.9	4.3	0.5	28.6
Decatur	46.5	41.2	9.5	2.0	0.8	21.5
Joliet	31.9	43.9	21.1	2.3	0.8	27.8
Rock Island	44.9	34.0	14.4	5.6	1.1	25.0
East Moline	37.2	51.3	9.4	2.0	0.0	23.5
Harvey & Phoenix	44.7	38.9	13.3	2.2	0.9	22.6
E. Chgo. Hgts.	25.0	61.0	12.8	0.6	0.6	27.3
Chicago Hgts.	38.0	42.6	16.0	3.0	0.4	25.2
Robbins	41.7	45.6	12.6	0.0	0.0	22.2
Carbondale	22.3	61.0	15.2	1.1	0.4	28.5
Rockford	48.6	41.8	8.4	1.1	0.2	19.8
TOTAL	36.9%	44.5%	14.8%	3.1%	0.8%	25.5%

Table 3

% OF CHILDREN HAVING BLOOD LEAD VALUES IN THE FOLLOWING 20 MCG.% RANGES

CITY	0 - 19 Mcg. %	20 - 39 Mcg. %	40 - 59 Mcg. %	60 - 79 Mcg. %	80 + Mcg. %
Aurora	37.9%	37.9%	16.9%	3.8%	3.6%
Springfield	21.5	48.4	23.0	6.1	1.0
Peoria	22.0	46.8	22.2	7.5	1.6
E. St. Louis	30.1	45.2	19.9	4.3	0.5
Decatur	46.5	41.2	9.5	2.0	0.8
Joliet	31.9	43.9	21.1	2.3	0.8
Rock Island	44.9	34.0	14.4	5.6	1.1
East Moline	37.2	51.3	9.4	2.0	0.0
Harvey & Phoenix	44.7	38.9	13.3	2.2	0.9
E. Chicago Hgts.	25.0	61.0	12.8	0.6	0.6
Chicago Heights	38.0	42.6	16.0	3.0	0.4
Robbins	41.7	45.6	12.6	0.0	0.0
Carbondale	22.3	61.0	15.2	1.1	0.4
Rockford	48.6	41.8	8.4	1.1	0.2
TOTAL	36.9%	44.5%	14.8%	3.1%	0.8%

ment of the 1972 data is currently being completed. Preliminary analysis, has revealed some extremely interesting results. The percent of children screened who demonstrated blood lead values in excess of 40 mcg.% ranged from 5.5% to 13.5%. These figures are lower than the range reported during the 1971 campaign. Despite the apparent reduction in range figures, it is still alarming to note the significant percentage of children, randomly screened, who demonstrated elevated blood lead levels. Perhaps, a more meaningful and certainly a more significant finding which was demonstrated during the 1972 campaign was the fact that while the raw numbers of children (and therefore the relative percentage) with blood lead values equal to or greater than 40 mcg.% was somewhat lower in 1972, the mean blood lead values remained remarkedly similar between the two years. Analysis of the 1972 data indicates a mean blood lead value of 27.32 mcg.% (corrected to reduce influence of fluctuating sample size).

DISCUSSION

Over 81 percent of the children screened were found to have blood lead values below 40 mcg.% cutoff point established by the U.S.P.H.S. Approximately 18.6% of the children screened demonstrated blood lead levels indicative of undue absorption of lead while 0.8% were classified as unequivocal cases of lead poisoning according to the U.S.P.H.S. guidelines[1].It is interesting to note that if the distribution of blood lead values is lumped by 20 mcg.% groupings, nearly one-half of the children (44.5%) demonstrated blood lead values in the 20-39 mcg.% range, while only slightly more than a third (36.9%) showed values less than 20 mcg.%. This may indicate that previously accepted normal blood lead values may be in error. Earlier workers have suggested that the median blood lead level in urban populations ranges from 16 to 27 mcg.%[8,14]. Since the children in this program were substantially from the most "at risk" group, ages 1-6 and living in deteriorated housing, and since their median blood lead value was 24.1, the values cited for the median blood lead values for the general population may be excessive.

A marked digital preference for "zero's" and "five's" in the reporting of results has already been mentioned. The five most frequently appearing values were 20, 25, 30, 10 and 15 mcg.%. 50% of all values reported in the range between 0 and 100 mcg.% ended in either a zero or a 5, while such values represent only 20% of the possible reportable values in that range. Possibly, a sensitive digital recorder attached to the atomic absorption spectrophotometer unit would reduce the digital preference[1]. The authors wish to point out that there is much discussion and controversy about the many methods which "may" be used to determine lead levels in the body; recently, the urinary aminolevulinic acid test described by Davis et al [16] seemed to hold most promise as a quick, simple and inexpensive procedure. However, Blanksma et al[17] and Blumenthal[18] amply demonstrated that while the collection of urine is more convenient than the collection of blood, the reliability of the ALA test is open to question. In fact, in a comparative analysis of the two methods the correlation coefficient between the urinary ALA test and the blood lead test was determined to be 0.11. In that study, the percent of children that would have been missed if the urinary test was substituted for the blood test was 33%. Those findings lead the authors to conclude that urinary ALA is not a dependable screening test for childhood lead poisoning. Based upon these findings as well as an exhaustive review of literature it is our opinion that the blood lead analysis, although some-what more cumbersome, expensive and critical is the most reliable laboratory and screening method available.

CONCLUSIONS

The Surgeon General has estimated that upwards of 400,000 children across the nation may possibly have elevated blood lead levels[15].If the Surgeon General's estimate was based upon the previously accepted hypothesis that elevated blood lead levels are confined to major metropolitan areas, then it would seem that this estimation of the extent of the problem must be revised upward to include the large numbers of children outside of major metropolitan areas also affected. For as this study has shown, elevated pediatric blood lead levels do exist in considerable numbers in communities of intermediate population.

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MERCURY IN THE PLACENTA AND FOETAL MEMBRANES AS AN INDICATION OF LOW MERCURY EXPOSURE

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ABSTRACT

In order to evaluate the foetal load of mercury when mothers were exposed to elementary mercury, we have compared two groups of women and their babies at birth. One group consisted of dentists, dentists' assistants and dental technicians. The control group were arbitrarily chosen among other women delivering at the same hospital.

There were no differences between the groups in mercury content of erythrocytes or plasma in mothers or babies. Amnionic fluid also contained the same amount of mercury in both groups.

The placenta, the chorion-allantois membrane and the amnion membrane contained, however, significant more mercury in the exposed group than in the control group.

Thus the mercury content of the placenta, the chorion-allantois membrane and the amnion membrane might give an indication of excess mercury load to the foetus. This even with exposure levels that do not alter the erythrocyte or plasma content of mercury in the mothers or in the babies.

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1. Introduction

Placenta represents a barrier to **inorganic mercuric ions.(Friberg** and Vostal [1].) Elementary mercury will within minutes be oxidized to inorganic mercuric ion in the body, - however, it crosses the placenta while being in the elementary state. (Clarkson et al.[2].) In order to investigate if the babies of mothers occupationally exposed to low levels of elementary mercury had an increased mercury load, one group of dentists, dentists' assistants and dental technicians and one group of non exposed women were studied.

2. Material and Methods

The women in the exposed group were working in different dental offices in the Oslo region. No measurements of their workplace exposure were made, but from other studies (unpublished) the exposures are known to be around the TLV value (0.05 mg Hg/m^3) or lower. The non exposed group was arbitrarily chosen among other women delivering at the same hospital. At birth samples of the mother's and the baby's erythrocytes and plasma, the amnionic fluid, the placenta, the chorion-allantois and amnion membrane were taken for analysis of total mercury content. The samples were pyrolyzed and the mercury determined with atomic absorption. The Student's t-test was applied to evaluate the differences between the groups, and p values 0,0500 and less accepted as significant.

3. Results and Discussion

There was no difference between the groups in mercury content of the amnionic fluid. Neither were there any differences between the groups in mercury content of erythrocytes and plasma in the mothers or in the babies (Table 1). However, the blood content of mercury falls rapidly after exposure to elementary mercury, and blood is unreliable as a biological parameter for inorganic mercuric ion load in target organs.

The mercury levels in erythrocytes and plasma are similar to those previously found by Tejning [3] (8.6 ng Hg/g) in Sweden. Suzuki et al.[4] in Japan, however, found levels which were 2-3 times higher (22.9 ng Hg/g). Both found that the erythrocytes of the babies contained 30-50% more mercury than the mothers', while the plasma of the babies contained 10-20% less than the mothers'. The same tendencies appear in our results (Table 1), but the differences are not statistically significant (p = 0.42).

The exposed group has a higher mercury load in the placenta and in the foetal membranes than the control group. The values for the placenta are 24.47 ng Hg/g tissue and 12.00 ng Hg/g tissue, respectively (p = 0.0013), for the chorion-allantois membrane 21.61 ng Hg/g and 11.47 ng Hg/g (p = 0.0032) and for the amnion membrane 14.54 ng Hg/g and 5.32 Hg/g (p = 0.0134) (Table 1).

Table I. Total mercury content of tissues.

[+] The mean value and standard error of the mean are given in ng Hg/g tissue

	Control	Exposed	Student's t-test
Mother erythrocytes	7.96 ± 0.49 [+]	8.84 ± 0.87	p = 0,3520
Mother plasma	4.62 ± 0.48	4.63 ± 0.68	p = 0,9841
Baby erythrocytes	8.85 ± 0.74	10.18 ± 1.44	p = 0,3736
Baby plasma	4.31 ± 0.57	4.06 ± 0.66	p = 0,7741
Amnionic fluid	3.23 ± 0.39	2.33 ± 0.49	p = 0,3046
Placenta	12.00 ± 0.93	24.47 ± 4.06	p = 0.0013
Chorion-allantois membrane	11.47 ± 1.25	21.61 ± 3.38	p = 0.0032
Amnion membrane	5.32 ± 0.76	14.54 ± 4.12	p = 0.0134

The mercury content in the placenta of both groups, in both foetal membranes of the exposed and in the chorion-allantois of the controls is higher than in maternal and foetal blood. Thus both placenta and membranes might act as a "sink" for mercury. However, the importance of this "sink" function as protection for the foetus against mercury is not known. Neither is it known if the mercury load will alter the function of these organs, thus impairing the conditions for the foetus. Garrett et al. [5] and Wannag (unpublished) injecting pregnant rats with ^{203}HgCl, found mercury to accumulate in the placenta and in the foetal membranes while little entered the foetus. The accumulation was larger in the chorion-allantois than in the amnion, similar to humans. This in contrast to the greater binding capacity for mercury by the amnion in vitro. The in vivo/in vitro difference might be caused by the better blood supply to the chorion-allantois which should give this membrane a higher mercury exposure than the amnion.

4. Conclusion

Even with an exposure level of elementary mercury which do not alter the mercury content of blood in mothers or babies, the placenta and the foetal membranes get an increased load of mercury. This reflects an increased mercury exposure to the foetus, and the mercury levels in the placenta and foetal membranes might give an indication of the mercury load in foetal target organs. However, no study of the mercury content in foetal organs has yet been undertaken.

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DISCUSSION

ROELS (Belgium)

1. Concerning the blood in the placenta, what pretreatment did you apply to remove it?

2. What is the contribution of blood-mercury to the values you measured in the placenta's?

WANNAG (Norway)

1. No specific: the tissue pieces were squeezed to get as much as possible of the blood out, they were washed in deionized water.

2. As we don't know the exact amount of blood - we naturally don't know the amount of Hg which comes from the blood. However, the Hg blood valves (normal group: erythrccytes 7.96 ng HG/g and plasma 4,62 ng Hg/g) are lower than that of the placenta (12,00 ng Hg/g). Thus the "contamination" of blood in the placenta in this case lowers the calculated result for Hg in the placenta tissue.

CERNIK (U.K.)

What volumes of blood was required for the analysis of mercury in the unexposed control group. Also which method of analysis was used? Flameless AAS with reduction?

WANNAG (Norway)

Around 1 g, both of erythrocytes and plasma was pyrolyzed.

The Hg from the pyrolyzed tissue was collected in permanganate, from which it was driven of by stanous chloride and analyzed in AAS. However, I am sorry that I can not give the technical details of the AAS analyses as the analytical side of this study was taken care of by our department of chemistry.

ROSIVAL (Czechoslovakia)

How large was in your study the exposed and control group of women?

WANNAG (Norway)

Exposed group 19 women, nonexposed group 26 women.

BERLIN (C.E.C)

What was the range of mercury values observed in the various tissues and how were these values distributed?

WANNAG (Norway)

I am sorry I cannot give the range here accurately, as I do not have all the data with me. However, from the standard errors of the means found in table 1, it can be seen that the range is quite large and naturally most so for the exposed group.

No analysis of the distribution of the values has been made.

LAUWERYS (Belgium)

Do you have any information about the chemical forms of mercury in the placenta of both groups?

I suppose they could be quite different. In the control group mercury is probably mostly under the organic form (methylmercury e.g.); in the group exposed to mercury vapor, a certain proportion of the accumulated mercury could be inorganic mercury.

WANNAG (Norway)

No, only total mercury was analyzed. However, we hope soon to be able to analyze the different mercury compounds separately. The different compounds are in fact what really interests us, as the different mercury compounds have different toxicokinetics and toxicodynamics. I feel the time is overdue to talk about "Mercury" meaning total mercury, what we should talk about is the specific mercury compounds like - elementary mercury - inorganic mercury - methyl mercury, and so forth and keeping these distinctly appart.

ERFORDERNISSE IM HINBLICK AUF MESSUNGEN
MONITORING NEEDS
BESOINS EN MATIERE DE MESURE DE L'EXPOSITION
NECESSITA' RELATIVE ALLA MISURA DELL'ESPOSIZIONE
EISEN VOOR HET TOT STAND BRENGEN VAN TOEZICHT OP EXPOSIE

(Continued)

Vorsitzender - Chairman - Président - Presidente - Voorzitter

J. BOUQUIAUX (Belgique)

ESTABLISHING SAFE AMBIENT AIR QUALITY LEVELS FOR EIGHTEEN HAZARDOUS POLLUTANTS

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ABSTRACT

The central objective of this study was to provide data for the development of safe ambient air quality levels for eighteen hazardous pollutants, including thirteen metals, asbestos, boron, chlorine, fluorides and selenium. This proposed safe level for each pollutant was then compared with the magnitude and pervasiveness of that pollutant to provide insight for planning and developing hazardous pollutant control technology. An additional value of these proposed safe concentrations is to provide input to the current U.S. Government effort to establish official safe levels of pollutants in the air.

The principal effort in gathering the data for developing safe levels consisted of an in-depth investigation conducted through personal contact with twenty three recognized experts in the epidemiology of air pollution from the medical and public health professions. The investigations were designed to provide the most current integrated opinion on this subject. An analysis and discussion of the results are presented. In addition, a comparison is shown between these results and ambient air quality standards which have been established by several nations and various states in the U.S.

A comparison among the tonnage of pollutant emitted, the population in areas adjacent to the major emitter, and the safe

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ambient air quality level was made in order to indicate priorities which should be established for research and development of control technology for these pollutants.

This paper presents the results of two small parts of a much larger study performed for the U.S. Environmental Protection Agency. Obviously the data presented here must be brief and in summary form. Information on all the other aspects of the study is available from the authors.

1. Introduction

In order to establish safe ambient air quality (AAQ) levels, it is necessary to determine a measure of toxicity to humans for the pollutants under investigation. These relative toxicity values can then be used to define safe rates of inhalation of the elements and compounds and, thus, to estimate safe AAQ levels. If toxicological information were complete for the concentrations generally found in the ambient air, and if this information included data on the effects of these concentrations on the entire population, a safe AAQ level for each pollutant could be set with confidence. Unfortunately, not only are the required data unavailable, but necessary analytical techniques are beyond present capabilities.

Ideally, the final setting of a safe or tolerable AAQ level for each pollutant would result from a thorough understanding of the varied effects on humans at all stages of development as they are exposed to different combinations of pollutants, the synergistic effect of pollutants, the changing effects of pollutants as they are chemically altered with changing weather, and the reinforcement of an airborne pollutant's effects when the same material is ingested. However, the determination of estimates of safe concentrations of pollutants in the ambient air demands an extension of known data into a realm of great uncertainty.

2. Presumed Safe Ambient Air Quality Levels

Experience, intuition, analysis and information must all be used to arrive at best possible estimates of levels of pollution that will not prove harmful to man. This has been done in the course of this study. Existing relevant data have been assimilated from literature and personal interview, and are presented in Table I for each of the eighteen hazardous pollutants studied.

The information presented includes first, maximum concentrations measured in the ambient air, second, the average of expert estimates on the 24 hour maximum safe ambient air quality level, third, the average of existing ambient standards, and finally, threshold limit values.

The estimates of presumed safe levels shown in the table represent the average opinion of the following six experts in the field of air pollution and human health who suggested numerical estimates:

1. Dr. H. A. Schroeder, Dartmouth Medical School
2. Dr. H. E. Christensen, National Inst.for Occupational Safety and

health.

3. Dr. H.B. Elkins, Commonwealth of Massachusetts, Division of Occupational Hygiene
4. Dr. B. Ferris, Harvard School of Public Health
5. Mr. G. Boylen, Industrial Hygiene Office, Massachusetts Institute of Technology
6. Dr. G. Gordon, Department of Chemistry, University of Maryland

These experts in the field of epidemiology of air pollution and toxicity took experimental results, statistical data, and subjective philosophies of life into consideration to arrive at meaningful, safe AAQ levels. Not all of the estimates for each pollutant are the same; not all of the experts have identical bases for their opinions. However, the averages shown should provide a good basis for further investigation.

3. Population Affected

Table II presents data showing the total annual emissions for each of the hazardous pollutants, the major emitters of these pollutants and the annual emissions from these sources. Also shown are the number of cities where these major emitters are known or estimated to be and the adjacent population. The annual emissions shown are for the U.S.A. in 1968. The adjacent population figures were calculated by assuming that all persons in the city where an emitter was located were potentially exposed. However, an exception was made for very large cities or metropolitan complexes where an upper limit of one million persons per location was used. These figures are intended only to give gross indications of the population affected and should not be considered immutable.

It is quite clear that the largest segments of the population are affected by emissions from both coal and oil burning utility plants and residential fuel oil combustion. However, it does not follow automatically that these emitters deserve first priority for future research and control. The relative toxicity of the emissions must also be taken into account by comparing the average safe AAQ level with typical AAQ values found in the areas surrounding the major emitters. Unfortunately, sufficient data does not exist to clearly establish existing AAQ values, and it is possible only to indicate the approach which should be taken. For example, the safe level for tin is shown in Table I to be 13.7 $\mu g/m^3$ and a typical AAQ value for tin in a steelmaking city is 0.01 $\mu g/m^3$. Thus the safe level is three orders of magnitude greater than the observed level. In a similar

TABLE I

Ambient Air Quality Values for Potentially Hazardous Pollutants

($\mu g/m^3$ except as noted)

Pollutant	Urban/Non-Urban Values Maximum Observed	Average Experts 24hr Safe Level	Average of Existing Ambient Standards	TLV ÷ 100 Workweek Time-weighted
Arsenic	---	5.9	3	5 arsenic and cpds. 2 arsine
Asbestos	---	.05 fiber/ml	---	.05 fiber/ml longer than 5μ
Barium	1.50/0.00	77.5	---	5
Beryllium	.002/.00019	.005	.01	.02
Boron	---	50	---	100 B_2O_3 & BBr_3 30 BF_3
Cadmium	.37/.043	1.2	---	1 oxide fume 2 sol.salts & dust
Chlorine	---	30	30	30 Cl_2; 3 ClO_2 70 HCl; 4 ClF_3
Chromium	.10/.270	4.6	1.5	1 CrO_3;5 sol.salts 10 metallic and insoluble salts
Copper	1.20/.25	10	--	1 fume;10 dust
Fluorides	1.89/.16	47	8.1	20 HF;25F; 2 F_2
Lead	16.00/.20	4.7	1.0	1.5 lead arsenate 2 others
Manganese	1.44/.08	11.4	10	50
Mercury	---	0.8	0.3	.1 alkyls;.5 others
Nickel	.42/.76	3.7	--	.07 nickel carbonyl 10 others
Selenium	---	5.4	--	4 selenium fluoride 2 others
Tin	.10/.01	13.7	--	1 organic;20 inorg.
Vanadium	1.30/.024	6.8	2	.5 fume;5 dust V_2O_5
Zinc	2.80/.77	34	--	50 ZnO; 10 $ZnCl_2$

Table II

Population Affected by Major Emitters of Hazardous Pollutants

Pollutant	Total Emissions (tons/yr)	Major Emitters	Tons/yr Emitted	Number of Locations	Adjacent Population (millions)
Arsenic	9268	agric applications primary Zn roasting	2925 1390	no estimate 17	no estimate 0.5
Asbestos	6261	mining	5610	9	negligible
Barium	10,826	Ba chemical mfg milling & handling	4400 2700	11 7	1.1 0.8
Beryllium	144	utility coal boilers	101	325	at least 15
Boron	9520	utility coal boilers B chemical mfg	3055 2400	325 54	at least 15 no estimate
Cadmium	2305	iron blast furnaces	1000	45	5.6
Chlorine	78,200	liquefaction & handling	43000*	58	5.7
Chromium	12,006	utility coal boilers Cr alloy production	6425 4200*	325 16	at least 15 1.3
Copper	13,463	primary Cu converters	3729	19	0.6
Fluorides	163,140	utility coal boilers steel open hearth	28,384 25,400	325 64	at least 15 8.6
Lead	9,000	secondary Pb smelters gray iron foundary	2,000 1,400	56 1680	17 no estimate
Manganese	18,993	ferro-alloy electric furnaces	3,669	53	no estimate
Mercury	793	application of paints utility coal boilers	215 173	no estimate 325	no estimate at least 15
Nickel	6,233	residential fuel oil utility oil boilers	2,435 1,441	14429,250 122	at least 40 at least 13
Selenium	855	utility coal boilers glass manufacture	413 203	325 249	at least 15 no estimate
Tin	356	steel open hearth	260	64	8.6
Vanadium	18,873	residential fuel oil utility oil boilers	8,330 4,930	14429,250 122	at least 40 at least 13
Zinc	150,515	steel open hearth primary Zn roasting	39,000 31,818	64 17	8.6 0.5

*Before controls; all others after existing controls, if any.

way the safe level for beryllium is 0.005 $\mu g/m^3$ while a typical AAQ in a city with a coal burning utility plant is 0.0003 $\mu g/m^3$. Here the safe level is only one order of magnitude greater and if other factors are assumed equal, the beryllium emitter should have priority over the tin emitter for future study and control.

Therefore, the establishment of priorities for future action should be based on both the number of people exposed and the relative toxicity of each pollutant in the ambient air.

In this study it has been our objective to indicate in a gross way the average expert opinion on twenty-four hour safe levels. We have also given estimates of the pervasiveness of hazardous pollutant emissions in the U. S. A. The work is only beginning and we invite others to join us in the study of this very important area of air pollution research and development.

DISCUSSION

HÖGGER (Switzerland)

Did the speaker take particle size into account when evaluating airborne particulates and their deleterious effects on man? We know that with many substances particle size can determine how far the effects are harmful.

KEITZ (U.S.A.)

The toxicity of the various pollutants relative to their particle size was not within the preview of this study. Since it would be rather difficult to set ambient air quality standards based on particle size the Environmental Protection Agency did not ask for this type of information. We agree that such information is of great importance in hazardous pollutant studies and such studies should be undertaken.

DEN BOER (Netherlands)

You gave us the averages from the experts 24 h safe levels. How close were their levels together; what were the maximun and minimum values?

KEITZ (U.S.A.)

The spread of this data varied greatly among the various pollutants. In the case of barium compounds it was an order of magnitude. For beryllium the spread was very narrow. Information on this subject is much more detailed in our complete study which is available on request from the authors.

LEUNG (U.S.A.)

In obtaining the expert estimates, how the solicitation was done? Was it by personal interview, group interview, or by questionnaire that each expert has to provide written answers separately? If questionnaire was used, please describe the questionnaire briefly. Was any statistical analysis made to determine the group estimates dispersion, and to ascertain "the trustworthiness" of these experts estimates?

KEITZ (U.S.A.)

The experts were interviewed singly by personal contact. There was no formal questionnaire. Infact out of a total of 23 experts who were interviewed only 6 were willing to give numerical opinions.

The others did not desire to state numerical ambient air qualities. Due to the small sample size statistical analysis was not done. The dispersion of estimates was large for some cases and small for others. Information on these details is available from the authors on request. The "trustwortheness" of the estimates resides solely in the credibility and professional reputation of each of the experts. We feel that an excellent group was interviewed.

METHOD FOR THE IDENTIFICATION OF ENVIRONMENTAL NOISE LEVELS TO PROTECT PUBLIC HEALTH AND WELFARE

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ABSTRACT

This paper deals with environmental noise exposure affecting the public health and welfare and proposes a uniform, predictable, and easily measured method for characterizing the impact of environmental noise on public health and welfare independently of the noise sources. The concept serves as the basis for the definition of safe noise exposure levels.

1. Introduction

The purpose of this paper is to discuss a method for assessing environmental noise and to identify levels which are protective of public health and welfare. The philosophy behind this work can be summarized in three statements: (1) discussion of public health makes sense only in terms of the total noise exposure sustained by the public; (2) desirable levels of noise from each source, and the duration of people's exposure to these levels, must be derived from the desirable maximum noise from any source to which the public may be exposed without undue effects on health; (3) identification of long-range noise goals requires that one method be used to characterize the impact of environmental noise independently of the noise sources which contribute to environmental noise.

Implicit in the above, is the requirement that any given noise exposure be predictable and verifiable through measurements by the same yardstick as any other noise exposure so that the total cumulative noise exposure of people be obtainable, irrespective of where or under what conditions these exposures are sustained.[1,2]

Thus, a tool emerges which may neglect some details in the measurement of noise for simplicity and uniformity sake. However, so long as the agreed upon method is easily translatable to other more detailed and hence complicated measures, details may be best taken into account in procedures associated with emission standards. This development represents a step forward in the noise field since the lack of progress in noise abatement may have been due to the absence of a simple, uniform, predictable and inexpensively monitored scheme for assessing noise impact.

2. Methodology for Specification of Environmental Noise

The accumulated evidence of research on human response to sound indicates that the magnitude of sound as a function of frequency and time are the basic indicators of human response. This consideration, combined with the philosophy presented above, has led EPA to choose the equivalent A-weighted sound level, L_A, in decibels as its basic measure for environmental noise. Its basic definition is:

$$L_{eq} = 10 \log_{10} \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} 10^{L_{A(t)/10}} dt \qquad (1)$$

where $t_2 - t_1$ is the time interval over which the levels are evaluated.

This equivalent sound level is the constant sound level which, in a given situation and time period, would convey the same amount of energy to the ear as does the actual time-varying noise pattern. Thus, two sounds, one of which contains twice as much energy as the other but lasts only half as long as the other, would convey the same amount of energy to the ear and would be characterized by the same sound level.

This concept is not new and has been utilized to describe the onset and progression of Noise Induced Permanent Hearing Loss (NIPTS).[3] Furthermore, there is evidence that something much like it relates to the general adverse reaction of people to noise.[4]

Thus, EPA has evolved the Day-Night Sound Level, L_{dn}, to describe the noise climate in those environments in which individuals are expected to be present for prolonged periods of time such as residential dwellings. Other schemes have been proposed such as NEF, CNR, NPL, etc.; however, these schemes are much more complicated, often more limited in application, difficult and expensive to monitor, while not significantly increasing the accuracy of predictions.

The primary interval of time of interest in L_{dn} is the 24-hour period. Community measurements have shown that during the nighttime, exterior background noises generally drop in level from daytime values. Also, the activities of most households decrease at night, thus, lowering the internally generated noise levels as shown in Figure 1. As a result, intrusive noise events become more noticeable at night. These differences are accounted for by applying a penalty to noise events occurring at night, that is, by treating nighttime noises as if they were several decibels noisier than they actually are.

For any reasonable distribution of environmental noise levels, a 2-period day and a 3-period day yields identical levels within a

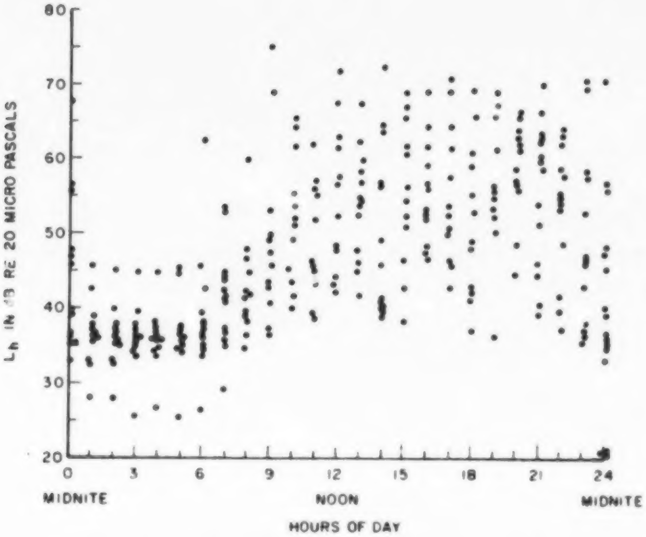


Figure 1. Noise Inside Living Areas of 12 Homes - Values of Hourly Equivalent Sound Level as a Function of Hour of Day.

few tenths of a decibel. Therefore, in the development of L_{dn}, the 24-hour day has been divided into a 2-period day with the day extending from 7:00 a.m. to 10:00 p.m., and the night period extending from 10:00 p.m. to 7:00 a.m. the next day.

To actually arrive at a magnitude of the penalty, an examination was performed of the diurnal variation in the equivalent noise levels during the day, L_d, and during the night, L_n, as a function of L_{dn}. Examination of a set of 63 community measurements spanning environments ranging from the quiet wilderness to the noisiest areas around airports and highways was utilized. This set of data is shown in Figure 2. It can be seen in Figure 2 that in quiet environments ($L_{dn} < 55$) L_d is the controlling element in determining L_{dn} because of the reduction in noise levels at night, usually around 10 dB, while in noisier environments ($L_{dn} > 65$) the values of L_n are only 30 to 4 dB below daytime values. Thus, a 10 dB penalty was chosen which applies pressure towards an around-the-clock relief in noise reduction. The actual equation for L_{dn} is:

$$L_{dn} = 10 \log_{10} \frac{1}{24} \left[(15)(10^{L_d/10}) + (9)(10^{(L_n + 10)/10}) \right] \quad (2)$$

where L_d and L_n are the daytime and nighttime equivalent levels respectively.

To assist the reader, Figure 3 shows typical values of L_{dn} for various types of environments found in the U.S.A. together with corresponding subjective evaluations.

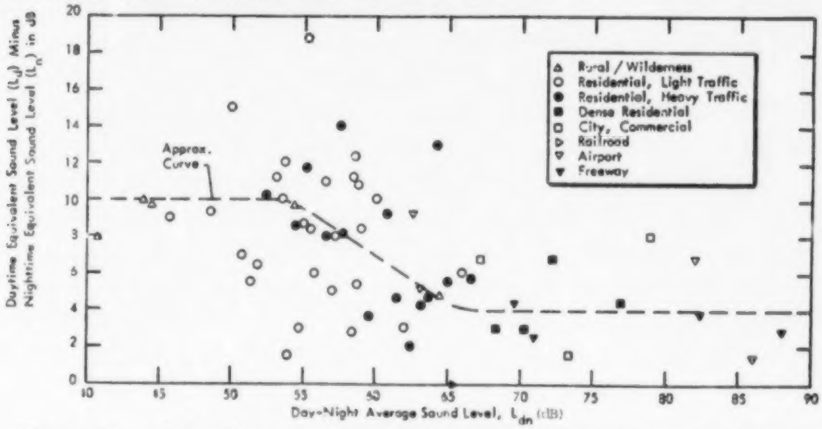


Figure 2. Comparison of the Difference Between Day and Night Values of the Equivalent Sound Level with the Day-Night Average Sound Level, L_{dn}.

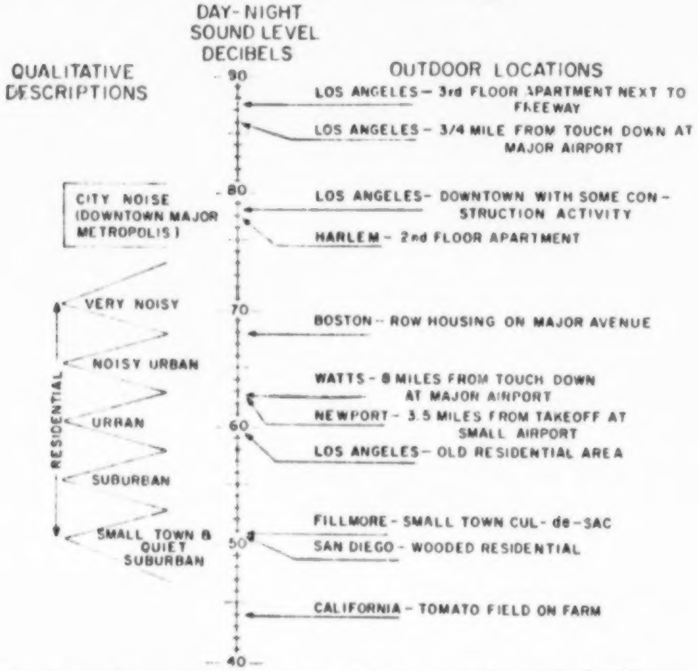

DAY-NIGHT SOUND LEVEL DECIBELS
QUALITATIVE DESCRIPTIONS
OUTDOOR LOCATIONS
90
80
70
60
50
40
LOS ANGELES – 3rd FLOOR APARTMENT NEXT TO FREEWAY
LOS ANGELES – 3/4 MILE FROM TOUCH DOWN AT MAJOR AIRPORT
CITY NOISE (DOWNTOWN MAJOR METROPOLIS)
LOS ANGELES – DOWNTOWN WITH SOME CONSTRUCTION ACTIVITY
HARLEM – 2nd FLOOR APARTMENT
VERY NOISY
BOSTON – ROW HOUSING ON MAJOR AVENUE
NOISY URBAN
RESIDENTIAL
WATTS – 8 MILES FROM TOUCH DOWN AT MAJOR AIRPORT
URBAN
NEWPORT – 3.5 MILES FROM TAKEOFF AT SMALL AIRPORT
LOS ANGELES – OLD RESIDENTIAL AREA
SUBURBAN
FILLMORE – SMALL TOWN CUL-de-SAC
SMALL TOWN & QUIET SUBURBAN
SAN DIEGO – WOODED RESIDENTIAL
CALIFORNIA – TOMATO FIELD ON FARM

Figure 3. Examples of Outdoor Day-Night Sound Level in dB (re 20 micropascals) Measured at Various Locations Throughout the U.S.A.

3. Long Range Goals for Environmental Noise Levels

3.1 General Approach

An ideal approach to establishing criteria for environmental noise levels in terms of their effects on the long-term public health and welfare would be to start by establishing the cumulative noise dose which an individual, or a population, may sustain over a lifetime without undue effect, irrespective of where or under what situation this exposure is received. This approach has been taken whenever possible. There are, however, many difficulties:

(a) The dose which an individual accumulates is a function of his life style. For example, exposure patterns of office workers, housewives and school children are quite different. Furthermore, within each group the exposure varies widely as a function of working, recreational and sleeping habits. Thus, two individuals working in the same office accumulate different total doses depending upon where they live, how they commute, and their TV habits. Examples of such variations are shown in Figure 4 - 6.

(b) There is little information on the statistical distribution of actual doses and the relationships to long-term health effects except for two selected situations: (1) the long-term effects of occupational noise exposure on hearing; (2) the average long-term exposure to noise in residential areas leading to annoyance and complaints.

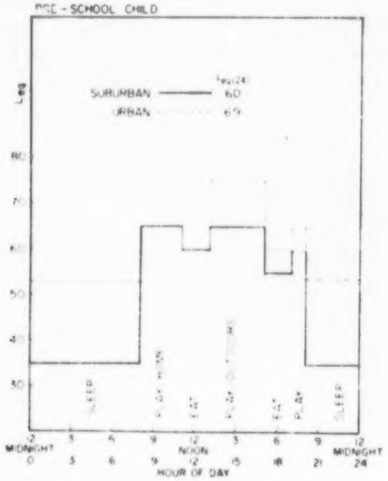


Figure 4. Typical Noise Exposure Pattern of a Pre-School Child.

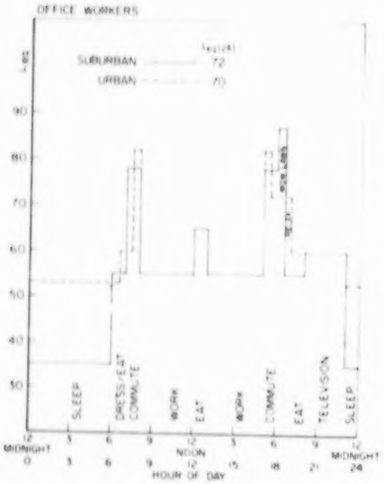


Figure 5. Typical Noise Exposure Pattern of an Office Worker.

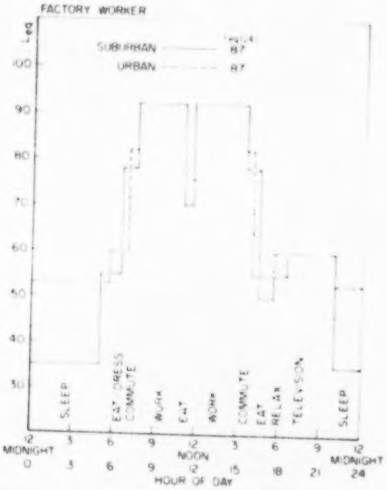


Figure 6. Typical Noise Exposure Pattern of a Factory Worker.

3.2 Goals for Hearing Preservation

To establish criteria for hearing, the hearing threshold of a noise-exposed population has been compared to the hearing threshold of a non-exposed population.[5] The analysis has been made in terms of the most noise sensitive frequency (4000 Hz) and the least amount of NIPTS which is measurable (5 dB). This approach represents a departure from traditional hearing criteria which are,at least in the U.S., predicated on averaged frequencies of 500, 1000, and 2000 Hz and a fence of 25 dB. These differences arise from EPA's concern with the total exposure of man rather than occupational exposure and problems related in occupational criteria developments to compensation for hearing damage incurred during work. The result of these analyses are shown in Figure 7. Inspection of Figure 7 reveals that virtually the entire population will be protected from any significant hearing loss if the noise dose does not exceed 73 dB over an 8-hour exposure.

Since most of the noise induced hearing loss data comes from occupational exposures, corrections were necessary to generalize the results to general environmental situations.

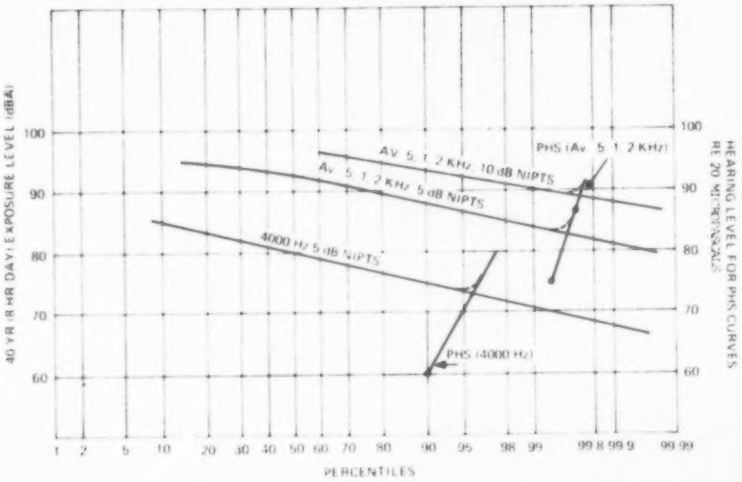


Figure 7. Exposure Level and Hearing Level as a Function of Population Percent Showing Merging of Different NIPTS Curves with PHS Curves.

(a) Most environmental noise is not continuous. Intermittent exposure is less damaging than continuous exposure; thus, the exposure level can be 5 dB higher than the dose identified.

(b) Since most of the data base is based on an average work year of 250 days, a -1.6 dB correction factor is applied to account for the total year.

(c) To account for the fact that a day is made up of 24 hours rather than 8 hours, a correction factor of -5 dB is also applied.

Thus, the yearly cumulative dose which will protect the general population from NIPTS is:

$$L_{eq} = 73 - 5 + 5 - 1.6 = 71.4 \cong 70 \text{ dB}$$

3.3 Goals for Environmental Noise with Respect to Activity Interference and Annoyance

The underlying concept in establishing goals for environmental noise has also been statistical. This is not to say that individuals have the same susceptibility; they do not. Even groups of people may vary in response depending on previous exposure, age, socio-economic status, political cohesiveness and other social variables. In the aggregate, however, the average adverse response of groups of people is predictable and related to cumulative noise exposure. The response we use is a combination of such factors as speech interference, sleep interference, desire for a tranquil environment and the ability to use telephones, radio, and TV satisfactorily.

In order to derive a dose-response relationship between noise exposure and human response, the results of the social surveys of the last 20 years have been examined. For the purpose of this analysis, and when possible, the noise levels in each survey has been converted to L_{dn}. The resulting relations are shown in Figure 8, together with a relationship showing the actual number of highly annoyed persons who actually lodge complaints.

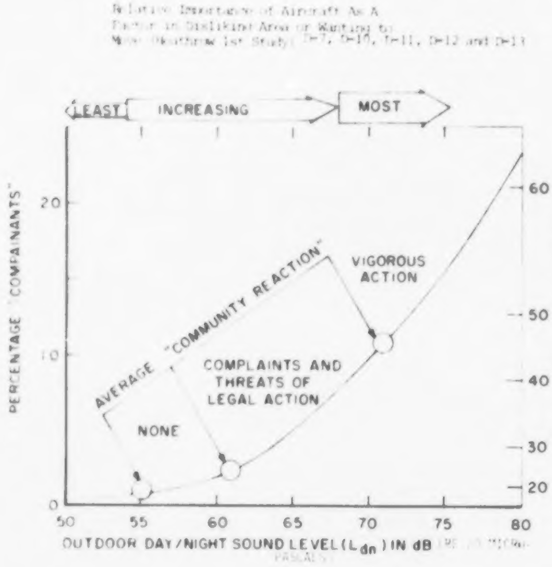
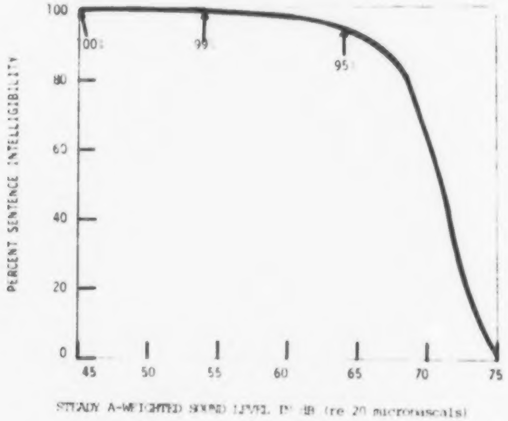


Figure 8. Summary of Annoyance Survey and Community Reaction Results.

For special uses such as schools and offices where criteria for speech communication is the primary concern, a similar averaging process is used to estimate the potential response of people as a group, again ignoring individual variations. Research since the 1920's has quantitatively characterized the masking effects of noise on speech perception. The effects of masking on speech perception indoors are summarized in Figure 9. This analysis assumes the existence of a reverberant field in the room and an acoustic absorption of 300 sabins typical of living rooms and bedrooms.



NOTE: Assumes 300 sabins absorption typical of living rooms and bedrooms and is valid for distances greater than one meter.

Figure 9. Normal Voice Sentence Intelligibility as a Function of the Steady Background Sound Level in an Indoor Situation.

3.4 Goals for Enviromental noise in Various Spaces and Land Uses

The above considerations lead to the specification for a variety of spaces and land uses of numerical values of noise levels which if not exceeded, would provide entirely acceptable acoustical environments from a public health point of view. These can be summarized in terms of yearly equivalent sound levels as follows: in residential areas, hospital and other areas where people are expected to be present for prolonged periods of time, an L_{dn} level of 45 and 55 dB for indoor and outdoor areas respectively; for areas where speech is of primary concern, an $L_{eq(t)}$ of 45 indoors, and for those areas where hearing protection is of primary concern, an $L_{eq(24)}$ of 70 dB irrespective of area.

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DISCUSSION

BERLIN (Sweden)

I have difficulties to accept your assumption that there is a simple relation between A-weighted average noise levels and the degree of disturbance of the population. I think the weight of the evidence in the literature is that the character and frequency of noise are at least as important as the level. What neurophysiological basis do you have for this assumption?

I also like to point out that according to our experience and acceptance of your standard would lead us into difficulties, e.g. noise from single aeroplanes, motorvehicules, trains etc. passing with a low frequency, can be as disturbing for the sleep in a quite area than a continuous noise of much higher A-weighted L_C value. We have positive evidence for that from investigations going on in our laboratory.

YANIV (U.S.A.)

I certainly would agree with you that the response of human beings to sound depends strongly on the frequency of sound. Two basic approaches can be utilized to account for these differences:

- one may divide the sound pressure spectrum into a series of contiguous frequency bands by electrical filters so as to display the distribution of sound energy over the frequency range;

- one may apply a weighting to the overall spectrum in such a way that the sounds at various frequencies are weighted in much the same way as the human ear hears them.

The first approach is employed in detailed engineering studies of noise sources. However, for monitoring purposes it is much too complicated. The second approach uses a special electrical weighting network in the measurement system. This network weights the contributions of sounds of different frequencies so that the response of the average human ear is simulated. Each frequency of the noise then contributes to the total reading an amount approximately proportional to the subjective response associated with that frequency. Measurement of the overall noise with a sound level meter incorporating such a weighting network yields a single number such as A-weighted sound level. For monitoring purposes this represents a marked simplification.

The bulk of the literature tends to support the position that the A-weighting is an adequate way to deal with the ear's differing sensitivity to sounds of different frequencies. Indeed, for many noises the A-weighted sound level has been found to correlate as well with human response as more complex measures such as calculated perceived noise level of the loudness level derived from spectral analysis.

(1) It is true that psychoacoustic research indicates that for some noises a different frequency weighting which increases the sensitivity to the 1000-4000 Hz region might be more desirable. (2) However, various forms of this alternative are currently in existence; none of these have yet progressed in acceptance to the point where a standard exists thus limiting its applicability for monitoring purposes at this time even though it might be more desirable.

The second major characteristic of noise is that it fluctuates considerably over time. Thus, one cannot simply say that the noise level at a given location or experienced by a person is that many decibels. To describe the noise completly one must use a method for accounting for the time-varying signal. A number of methodologies for combining the noise from both individuals events and quasi-steady state sources into measures of cumulative noise exposure has been developed: NEF, CNR, CNEL, NNI, PNL etc. Furthermore these methodologies while differing in technical details are in fact conceptually fairly similar and correlate well with each other. Also, the relationships between cumulative exposure and community annoyance also correlate well. (3-4) The equivalent sound level is formulated in terms of the equivalent steady noise level in a stated period of time that would contain the same noise energy as the time-varying noise during the time period. Again the bulk of the literature supports its use. In Germany it has been used to evaluate the impact of aircraft noise in the neighbourhood of airports. (5) In Austria it is used for evaluating the impact of street traffic on dwellings (6) and in schoolrooms. (7)

Research experiments by Pearsons on the trade-off of level and duration of noisy events (8) and other investigations of the trade off between the number of events and noise level in aircraft flyovers also support this approach.(9)

As to your second comment regarding sleep, I appreciate your concern which I share. Nevertheless, as you know there exists a very limited amount of consistant data regarding environmental noise effects on sleep. I do not know how one may handle this problem at this time except by limiting noise levels at night. Surely you cannot be implying that we raise background noise levels at night so as to reduce the effects of intrusive single events. To my knowledge the value to 32 dB that would result indoors at night from a level of 55 dB outdoors is consistent with the limited amount of criteria for sleep. However, as more data developes the method which we have proposed will be refined and revised.

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RELATIONSHIP BETWEEN ACUTE RESPIRATORY ILLNESS AND AIR POLLUTION LEVELS IN AN INDUSTRIAL CITY

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ABSTRACT

A retrospective study relating hospital admissions for acute exacerbations among adults with chronic respiratory illness, and among children with acute respiratory disease, to air pollution levels was carried out in a highly industrialized Canadian city.

Two thousand patient records were collated and daily, weekly and monthly averages for admissions to hospital were related to a contemporary standard air pollution index (A.P.I.) which takes into account particulate matter and SO_2*. A correlation coefficient of 0.53* ($P < 0.10$) *was found for the city as a whole, but the relationship was more marked where industry was most concentrated. Admission data from the hospital closest to the industrialized area showed a much higher correlation coefficient with A.P.I. (0.80,* $P < 0.05$*).*

Thus there is a strong relationship between A.P.I. and hospital admissions due to respiratory illness in a susceptible population.

(Supported by National Health Grant No. 215-6225 Government of Canada).

During the past decade several epidemiological studies have suggested a relationship between air pollution and morbidity or mortality due to respiratory disease. While there has been little doubt of the association during the notorious disasters which occurred in the Meuse Valley, London, England, and Denora,Pa., the association of health effects and exposure to lower, apparently acceptable levels of air pollution over long periods, remains a matter of some contention.

For this reason a retrospective study was done, which included all children and adults admitted to all of the hospitals in a highly industrialized city, for an acute respiratory illness or an acute exacerbation of a chronic respiratory illness during a period of one year. We were thus able to study a large patient population that varied in age, type of respiratory disease and domicile with respect to industry.

The aim of this study was

1. to establish correlations between hospital admissions for acute respiratory illness and an air pollution index,
2. to examine separate effects of sulfur dioxide and particulates as well as other common pollutants, and
3 to study the effects of meteorological factors.

Hamilton, Ontario, Canada's largest steel producing and one of its most polluted cities, lies at the south-west tip of Lake Ontario and has a metropolitan population of approximately 350,000. It is unique by virtue of the fact that there is a single point source of intense pollution - the steel factories and that it can be readily divided into four main districts each of which has a biological monitoring station, otherwise known as a hospital which, for the most part, serves the local district population. We will refer to these hospitals as A,B,C, and D. (figure 1). Hospitals A and B lie below a 300 foot plateau, 2.5 and 4.5 Km from industry, while C and D are on the plateau 3.5 and 8 Km away (figure 2). The single air pollution monitoring station is situated in the centre of the city at (P). For most of the year the prevailing wind is from the south-west.

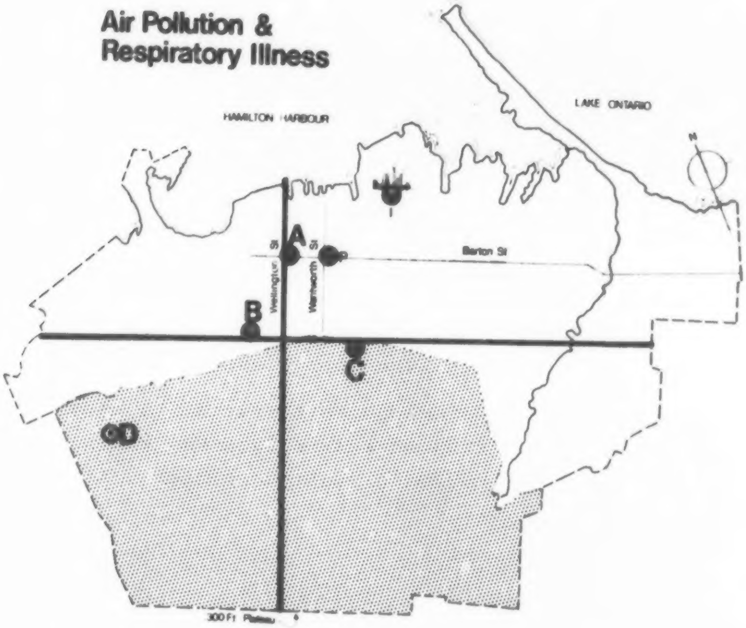


Figure 1 : Location of the smelter, air pollution measuring station and biological monitoring stations (hospitals) in Hamilton.

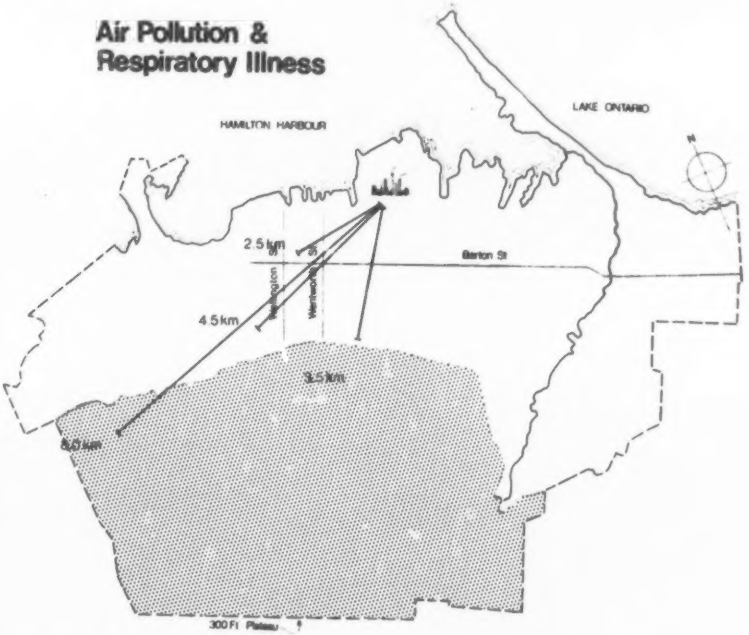


Figure 2 : Distance of biological monitoring stations (hospitals) from steel factories in Hamilton.

Patient selection was made by reviewing the charts of those admitted for acute respiratory illness (figure 3). After comparing the admitting and discharge diagnosis and evaluating the relevant clinical data, only those suffering from acute respiratory disease related to bronchitis, bronchiolitis, emphysema, pneumonia and asthma were chosen for this study. Only those patients whose histories revealed that they had suffered exacerbations of symptoms of shortness of breath, wheezing and cough within 5 days of admission were included. From approximately 5,000 charts reviewed only 1,780 were found to meet all of our criteria and these patients were then classified by age and sex.

Acute respiratory admissions were related to calculated Air Pollution Index, as well as sulfur dioxide, particulates, hydrocarbons, carbon monoxide, oxidants, pollens, temperature and humidity.

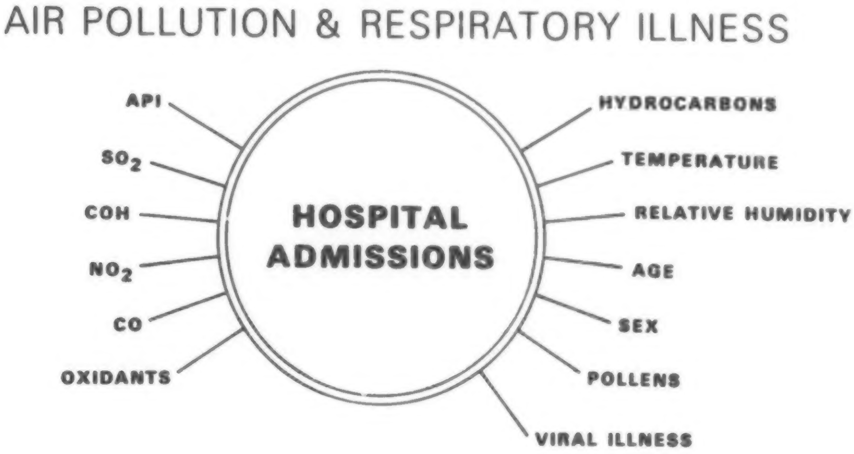


Figure 3

Figure 4 shows the formula used for calculating the API. It is obtained empirically using two components, sulfur dioxide and the coefficient of haze (or floating particulates) as its two variables. When the concentration of SO_2 is .1 parts per million and that of the coefficient of haze is 1 unit, the index is at our highest "acceptable" level of 32.

AIR POLLUTION & RESPIRATORY ILLNESS

THE AIR POLLUTION INDEX
IS OBTAINED FROM THE FOLLOWING EMPIRICAL FORMULA

$$\text{A.P.I.} = 2.5\,[13.9\ \text{C.O.H.} + 104.5\ SO_2]^{0.8}$$

C.O.H. = Coefficient of Haze
(OR Particulate Matter)

SO_2 = Sulphur Dioxide

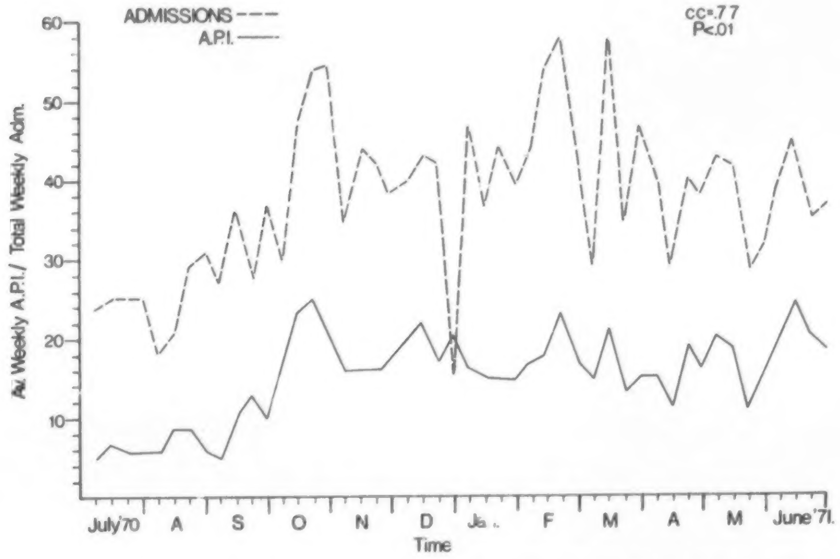
When C.O.H. = 1.0 and SO_2 = 0.1 ppm
Then A.P.I. = 32

Figure 4

Analyses of the air pollution index and the number of admissions were done on a daily, weekly and monthly basis and these two variables were related graphically. As previous studies had indicated that there is a 2 - 3 day lag between days of high air pollution index and admissions to hospital, we attempted to allow for this delay by looking at average weekly pollutant figures and total weekly admission.

Admissions fell broadly into a younger age group under 10 and an older group over 40, 65% of the number being male.

On graph 1 are plotted the total weekly admissions to all the hospitals and the average weekly air pollution index along the ordinate and time in months from July 1970 - June 1971 along the abscissa. This demonstrates that peaks and valleys in the air pollution index are generally reflected in the number of patients admitted to hospital - the most marked relationship appearing in October and February while the last week of December showed a striking disparity. The correlation coefficient describing this relationship was 0.77, highly significant at the 1% level.

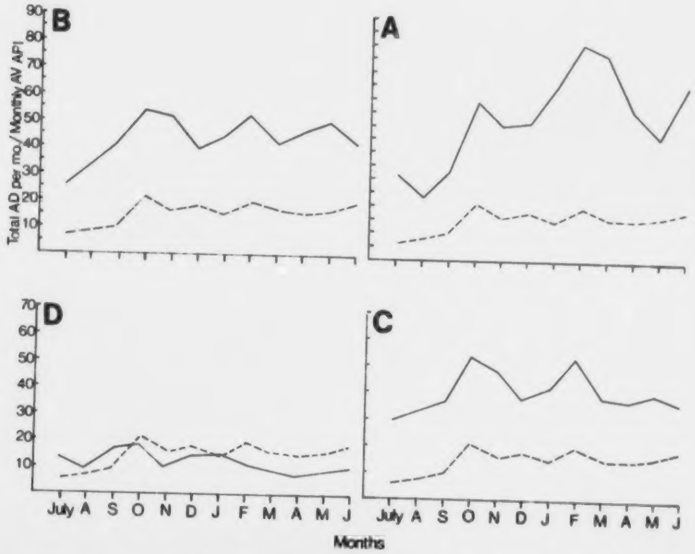


Graph 1 Total Weekly Admissions vs. Average Weekly A.P.I. for Whole City.

There are several additional points to note here. The air pollution index was higher on the average in 1971 than in 1970 and this was true also of the total number of admissions for respiratory illnesses. The peaks of both air pollution and hospital admissions in October and February were times of most frequent thermal inversions. Lastly, we noted a marked drop in admissions in the last week of December in spite of the high air pollution index. This is probably explained by the fact that this week encompasses both Christmas and New Years, a time when people like to remain at home, and this hypothesis was borne out by a sharp drop in the total admissions for all causes to each hospital during that week.

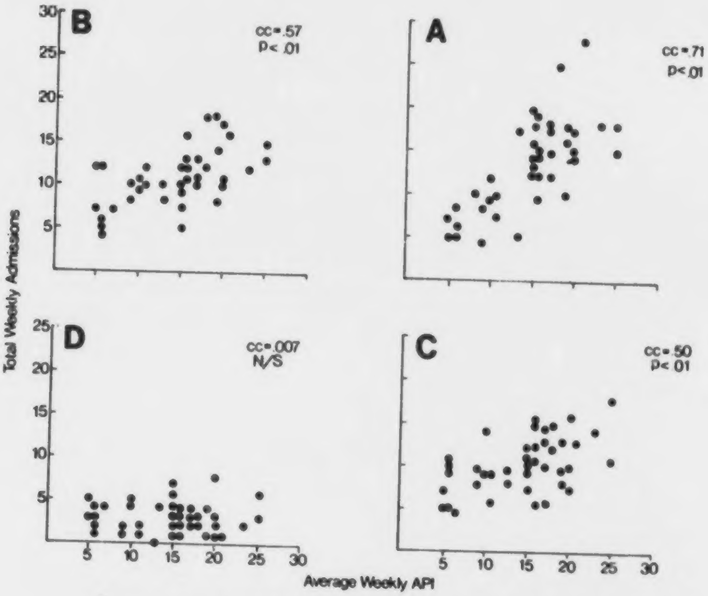
Having looked at the city as a whole, let us now examine each of the four regions by assessing admissions to the hospital serving that region.

On graph 2 are plotted the relationship between the average air pollution index and the total number of admissions per month at each district hospital as before. For hospitals A,B, and C, a similar relationship was found while no association was noted at D.



Graph 2 : Monthly Average API+Total Monthly Admissions vs. Time

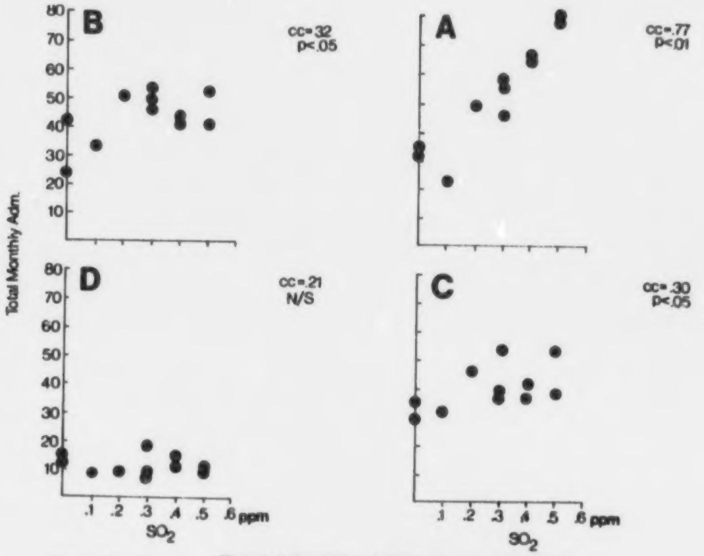
On graph 3 we see the relationship between total weekly admissions to each of the four hospitals along the ordinate and the average weekly air pollution index along the abscissa. We noted that the correlation coefficient measuring this relationship was highest at hospital A with a value of 0.71, 0.57 at hospital B and 0.50 at C, all measurements highly significant at the 1% level. The correlation coefficient at hospital D was .007 and not significant.



Graph 3 Average Weekly API vs Total Weekly Admissions for the four biological monitoring stations (hospitals)

Let us now examine the effects of the two individual components of the air pollution index, SO_2 and coefficient of haze, on admissions.

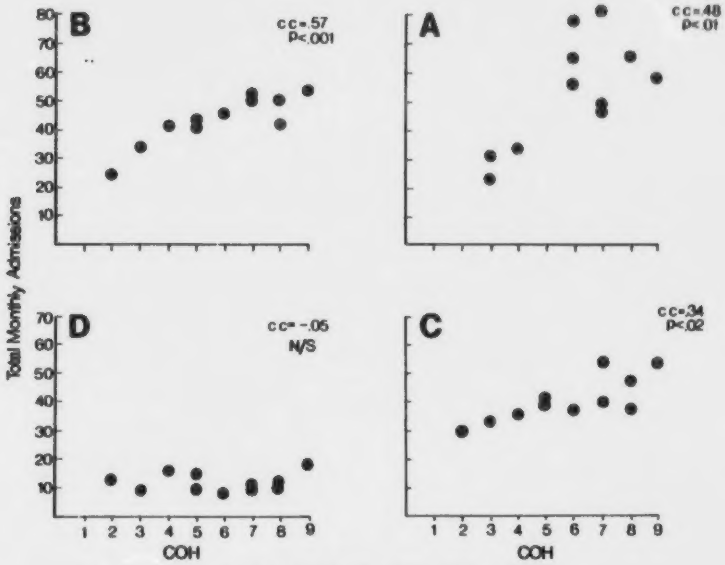
On graph 4 using the average monthly admissions along the ordinate we see a statistically significant correlation with SO_2 in tenths of a ppm on the abscissa in all hospitals except D. Here again hospital A showed the highest correlation.



Graph 4 : **Total Monthly Admissions vs. SO_2**
for the four biological monitoring stations (hospitals)

Graph 5 shows a significant correlation in all three hospitals between the number of admissions and the coefficient of haze. And again there was no correlation seen at hospital D.

When we looked at the other pollutants, carbon monoxide, oxidants and hydrocarbons, there was no correlation seen in any of the hospitals. When we examined the effects of pollens, temperature and relative humidity on admissions it was noted that while there was a moderate negative correlation with temperature, that is, more admissions on colder days, pollens and humidity appeared to have no effect.



Graph 5 : **Total Monthly Admissions vs.COH** for the four biological monitoring stations (hospitals)

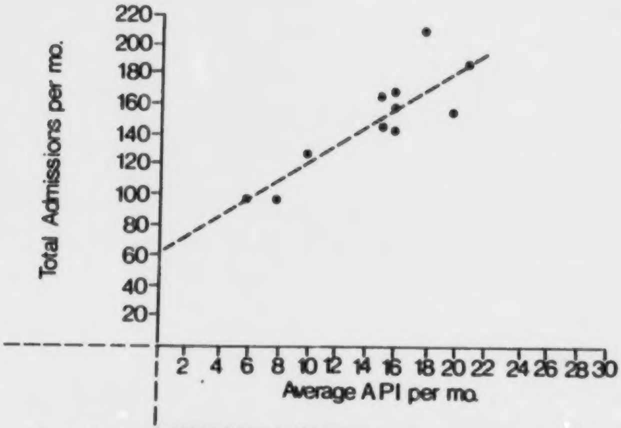
Discussion

Clearly the most important finding resulting from our study is the marked association between acute respiratory disease and the Air Pollution Index and its components, SO_2 and floating particulates for the whole city. This relationship is seen to be more marked the closer to industry patients live.

Furthermore, when other common pollutants were assessed, no association with respiratory illness could be found, suggesting that SO_2 and particulates are indeed most important in the pathogenesis of acute pulmonary disease due to air pollution and indicating the value of the calculated Air Pollution Index as it is presently determined.

If the monthly average for the Air Pollution Index is plotted against admissions for the 12 months of the study, a remarkably linear relationship is obtained which allows extrapolation to a "0" pollution level which predicts a basic pool of 60 admissions. When the mean Air Pollution Index for a month rises from 6 to 22, the "excess admissions" increase from 40 to approximately 120 - a 3-fold change which represents a more than 2-fold increase in the total admissions. (graph 6)

AIR POLLUTION & RESPIRATORY ILLNESS



Graph 6 **AVERAGE MONTHLY A.P.I. vs TOTAL MONTHLY ADM.**

Quite a definite age distribution was noted in this study. It is generally accepted that young children and adults past middle-age are more susceptible to illness. In this regard, our study supports similar work reported recently from both London and Chicago which showed that for a similar age distribution mild respiratory illness became more serious in the face of high pollution levels. The high proportion of male admissions might be accounted for by considering smoking habits and job exposure but these factors as well as socioeconomic conditions were outside the scope of our study.

The marked increase in admissions for respiratory disease in October and to a lesser extent February is a phenomenon well-known to chest physicians. Similar findings were reported by Lawther et al in London and this may relate to the unusually frequent thermal inversions at those times, accounting for higher pollution levels. In the studies of Lawther et al and Carnow, the reporting technique was inherently limited by the subjectivity of the responses. We think that by looking at hospital admissions in relation to an Air Pollution Index in this way, we have been able to introduce a measure of objectivity although we realize that we are merely observing the tip of an iceberg.

In conclusion, this study has shown:

1. A marked association between hospital admissions for acute respiratory illness and a calculated Air Pollution Index.

2 This relationship also holds true for the components of the Air Pollution Index, namely SO_2 and floating particulate matter as expressed in the coefficient of haze.

3 As indicated by the data from district hospitals, it appears that the correlation is greater at hospitals closer to industry.

4 Surprisingly, none of the other pollutants studied showed any relationship to acute respiratory illness.

5 While a reduction in temperature appeared to influence the incidence of acute respiratory illness, relative humidity did not.

DISCUSSION

STUPFEL (France)

During the time of collection of your data did you observe acute infectious episodes like influenza which could have been modified by the measured pollutant and meteorological parameter?

LEVY (Canada)

No. Unfortunately, from an epidemiological point of view, no viral endemies occurred during the study period.

GOLDSTEIN (U.S.A.)

In point 3 of your conclusions in which the correlation between air pollution levels and hospital admissions is greater at hospitals closer to industry (e.g. hospital A) are not these hospitals also closer to your single monitoring station than is hospital D which is furthest away from the monitoring station?

LEVY (Canada)

Since the pollution monitoring station was in the centre of the city, the city hospitals were, of course, closer to the single pollution monitoring station than hospital D. Within the city, however, hospital A (closest to both industry and the pollution monitoring station) had the highest correlation, while hospital B which was further away than hospital C (4.5 vs. 3.5 km) from industry (but below the plateau) showed a greater correlation.

Because of the prevailing wind (away from the hospitals + the monitoring station), the assumption of Lower Air Pollution levels at hospital D is a reasonable one. Hospital D was thus chosen as a "control."

MAGE (Danmark)

Considering the probability that the air pollution levels surrounding the only monitoring station are not perfectly correlated with the air pollution data you used and the correlation decreases with distance, how can you justify a study of this type when all your conclusions could be changed by moving your station by one kilometer?

LEVY (Canada)

While it is highly unlikely that the data from the single centrally located pollution monitoring station was completely representative of air pollution in districts represented by hospitals B and C, (and certainly was not representative of D), the city's geographical location (in a bowl), and prevailing wind, (from the southwest and lending to carry pollutants away from the population), would lead to an underestimate of maximum downwind concentrations and provides a reasonable "average"value (determined by spot sampling throughout the city.) Thus, in our situation moving the pollution monitoring station one or even more kilometers, while obviously producing an effect (higher if it were moved N.E., lower if moved S.W.) would be unlikely to change the air quality data greatly within the city. Even if one had a pollution monitoring station in each district, the same problem might arise. In spite of this, the fact remains that a very strong correlation exists between this "average" air pollution value and admissions for the city, a correlation which becomes "weaker" in proportion to the distance from the source of pollution. Clearly the more physical topographic pollution information available the better; however, as stated at the outset, in our context, 4 biological monitoring stations were available and indeed, from a health effects point of view, these appeared to be quite appropriate.

Fortunately, more physical monitoring stations are now being installed while at the same time industry is slowly improving pollution control. Our data will hopefully provide a baseline for future, similar, studies in our community to assess the beneficial health effects of this investment in pollution control equipment.

ENVIRONMENTAL CONTAMINATION BY AUTOMOTIVE LEAD

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ABSTRACT

For the past four years, an interdisciplinary team of researchers at Colorado State University has been studying environmental contamination by automotive lead. Reported in this communication are some of the major findings relative to monitoring the atmospheric component of the environmental flow of automotive lead.

A sampling technique which permits half-hour collection periods has been developed using low lead-blank porous graphite electrodes as filter media. Analysis by emission spectrography simultaneously provides data for other trace elements in atmospheric particulates.

Results of tests in which various membrane filters were backed by liquid scrubbers containing nitric acid indicate that these membrane filters allow a significant portion of the total atmospheric lead to escape collection. This deficiency may not be solely due to passage of organic lead; some lead reaching the scrubber is believed to be in the form of a very finely divided particulate. The implications are that many previously reported atmospheric lead values may be low and that many previously computed lead particle MMEDs may be high.

Field and wind-tunnel tests confirm that urban atmospheric lead levels are profoundly influenced by city geometry. Measure-

ment of Kr-85 concentration profiles in a scale model placed in a wind tunnel indicate that street canyons formed by two and three storey buildings, such as would be the case in a small town or in a suburban complex, can inhibit ventilation substantially. Moreover, under moderate crosswind conditions pollutant concentrations within the canyon are strikingly anisotropic, and street-level lead concentrations along the upwind building face are substantially higher than along the downwind face. Lead concentrations exceeding 10 $\mu g/m^3$ were measured in the street canyon while rooftop samplers indicated less than 1 $\mu g/m^3$.

The evaluation methodologies discussed are capable of providing considerable detail concerning the environmental flow of automotive lead and should be useful for other trace substances.

1. Introduction

The purpose of this communication is to report several new methodologies for quantitatively describing the environmental flow of automotive lead. The extent and significance of environmental contamination by automotive lead, both in terms of effects on human health and environmental effects, have recently come under intensive investigation in a number of countries where there is widespread use of lead alkyls as gasoline additives. While there is general agreement that man has substantially lead-contaminated some portions of his environment by combustion of leaded gasolines, scientific data are presently insufficient to adequately define the medical and environmental consequences (Commission of the European Communities [1], National Academy of Sciences [2]). For the past four years, an interdisciplinary team of researchers at Colorado State University has been studying the atmospheric component of dispersal of automotive lead in the environment. Summarized in this paper are recent findings concerning the dispersal and monitoring of automotive lead in the environment.

2. Atmospheric Sampling

Of critical importance to the accurate assessment of human exposures to airborne lead are effective sampling methodologies. The most commonly employed sampling technique involves drawing air through a membrane filter which is subsequently analyzed for lead. Two difficulties are now recognized. The first is that high lead blanks for many commonly used filter materials preclude short sampling times for lead levels found in typical urban atmospheres. Twenty-four hour sampling times are therefore commonly employed to swamp out the lead blank of the filter. These sampling times are far too long to permit correlation of observed atmospheric lead levels with short-term meteorological phenomena. The second difficulty is that a significant portion of the total atmospheric lead escapes collection by conventional filters (Purdue [3]). The portion that passes through the filter consists in part of organic lead compounds that reach the atmosphere through incomplete gasoline combustion and through gasoline leakages and spillages. A second portion of the nonfilterable lead may consist of very finely divided lead-containing particulates. Analysis of atmospheric particulates indicates that, of the metals ordinarily found in the atmosphere, only lead and vanadium are largely associated with submicron particles (Lee [4]).

A combined sampling-analysis method for the determination of trace elements in atmospheric particulates was developed by Skogerboe and Seeley as a part of this project (Skogerboe [5], Seeley [6]). Porous graphite spectroscopic electrodes are used as filter media; analysis for several elements is carried out using an emission spectrographic method. A major advantage is that the low lead blanks of the graphite electrodes permit much shorter sampling times, e.g., one-half hour with a flow rate of 800-1200 ml/min for atmospheric lead concentrations in the range of 1-10 $\mu g/m^3$. A second major finding of this work is that the porous graphite electrodes are more efficient for atmospheric lead than are a number of membrane filters. Experiments consisted of drawing air through a filter train in which various membrane filters were backed by the porous graphite electrodes. The tests demonstrate that the graphite filters collect about 5 % more lead than the membrane filters,on the average.

For other elements, including calcium, aluminum, and magnesium, the fraction passing through the membrane filter is normally substantially less, approximately a few tenths of a per cent of the total mass of the element collected. A third advantage of the graphite electrode sampling technique is the capability for simultaneous multielemental analysis.

Follow-up studies (Skogerboe [5]), in which membrane filters were backed by activated charcoal traps followed by liquid scrubbers containing nitric acid, indicate that membrane filter inefficiencies may not be solely due to passage of organic lead. Simultaneous atmospheric samples were obtained with the above filter trains downwind from a traffic source. The fractions of the total atmospheric lead collected in the train components, averaged for three determinations, are as follows: 0.45 μ membrane filter, 72%; activated charcoal adsorber, 5%; nitric acid scrubber, 23%. Lead found in the charcoal trap is tentatively designated organic, and lead found in the nitric acid scrubber may be ascribed to very fine lead-containing particulates which pass both the membrane filter and the charcoal trap. More elaborate tests are under way in an attempt to provide a clear distinction between the organic and particulate portions of the nonfilterable lead. Additional experiments, in which the charcoal traps were replaced with the previously described graphite electrode filters, confirm that some lead which passes through the membrane filter is caught in the graphite cup. These experiments also indicate that membrane filter efficiency for atmospheric lead decreases with increasing distance from the source. For example,

percentages of the total lead collected which were found on the membrane filters at various distances from the readway are as follows : 92 % at 2 m, 68 % at 28 m, and 66 % at 66 m. Thus, while use of membrane filter samplers alone would not lead to major errors in computing atmospheric lead burdens very near the source, atmospheric lead levels could be seriously underestimated at greater distances. If the smaller lead-containing particulates also escape collection by most inertial impactors used for particle sizing and the commonly used back-up membrane filters, the result could be a serious overestimation of lead particle sizes, particularly for samples taken beyond the region immediately adjacent to a roadway. These and other deficiencies of sampling techniques for atmospheric lead are under investigation by R. K. Skogerboe of this project.

3. Lead Dispersion in City Street Canyons

Human exposures to airborne lead from traffic exhaust tend to be greatest in city street canyons. Poor ventilation of city street canyons can have the effect in many cases of elevating pollutant concentrations substantially above the levels that would be predicted on the basis of standard diffusion equations. There is presently no totally satisfactory approach for mathematically modeling pollutant dispersion under these conditions. Physical modeling is presently the only effective technique for simulating street-level dispersion of atmospheric pollutants released from automotive exhaust in urban complexes. By means of physical modeling, the effects of local geometry of buildings, local topography, trees, and meteorological factors can be determined. Measurements are taken over a scale model of an urban complex in a wind tunnel in which various atmospheric boundary-layer conditions can be simulated (Cermak [7]). Concentration profiles of a radioactive tracer (Kr-85) released at "street-level" in the scale model are measured at various points to reveal pollutant dispersion patterns, and flow visualization is accomplished by observing movement of a smoke tracer. Physical modeling can therefore be highly useful for predicting the effects of a proposed new structure or traffic route upon local pollutant dispersion.

Physical modeling studies have been carried out within this project by Cermak, Lombardi and Thompson (Cermak [8]) to determine whether major lead concentration inhomogeneities could be expected in street canyons of Fort Collins, a medium sized town (population approximately 50,000). The geometry selected for modeling consists of a section along the main street which is lined by two and three-story buildings. Daytime traffic density averages 900-1000 vehicles per hour. The average lead content of gasoline sold in this area is 2¼ grams per gallon. In the laboratory model, uniform city blocks were constructed which measured 4Hx4HxH, where H is the model building height, 5 cm. Street widths are 1.5H in the present model. To simulate pollutant release from traffic on the four-lane street, the radioactive tracer was released at ground level from two parallel line sources in the street of the model. Air flows in the wind tunnel were thermally neutral.

The physical modeling studies to date reveal striking concentration inhomogeneities in the street canyons of the uniform geometry under moderate crosswind conditions. For pollutants released from two parallel ground-level line sources under 2 m/sec crosswind conditions, concentrations are higher along the upwind building face than along the downwind building face. On the upwind side, relative concentrations decrease from approximately 5 at street level to approximately 2 at H. On the downwind side, relative concentrations decrease from approximately 1.2 at street level to approximately 0.4 at H.

Field measurements in downtown Fort Collins provide qualitative confirmation of the wind tunnel measurements, notwithstanding some important differences between the present physical model and the actual street canyon geometry (Katen [9]). The height of the two and three story buildings forming the street canyon averages 9 m, and the actual street width is 42 m. With a 2.3 m/sec wind from the northeast (the street runs north-south), lead concentrations along the east side of the street canyon ranged from 11.3 μg/m^3 at street level to 4.0 μg/m^3 at roof level. On the west side of the street, lead concentrations ranged from 0.9 μg/m^3 at street level to 1.3 μg/m^3 at roof level. Vertical measurements along a light pole in the center of the street (a parking area) ranged from 3.7 μg/m^3 at street level to 1.4 μg/m^3 at roof level. Simultaneous measurement of atmospheric CO levels at each of these points suggests that vertical concentration gradients are steeper for Pb than for CO. CO levels are also higher along the upwind building face than along the downwind building face. Data from two additional sampling points above the rooftops on each side of the street are as follows: east side, 0.4 μg/m^3; west side, 0.9 μg/m^3. Correspondingly, above-rooftop CO levels were higher on the downwind side under these conditions. Additional measurements in nearby residential areas confirm that atmospheric lead concentrations decay rapidly with increasing distance from this source; lead concentrations 2-5 blocks away were in the range of 0.1 to 0.3 μg/m³. A detailed physical model is presently under construction to permit more quantitative correlation with field data. Additional field studies are underway to measure the nonfilterable portion of the atmospheric lead content at various points, both in the street canyon and in the surrounding residential areas.

4. Conclusions

Use of porous graphite spectrographic electrodes for air filters overcomes the high lead blank problem of many conventional membrane filters and thus enables ambient lead levels to be monitored for relatively short time periods. A second deficiency of many membrane filters is that in addition to organic lead, very fine lead-containing particulates may escape collection. These small particulates may comprise a significant portion of the total atmospheric lead content. Reexamination of many previously reported airborne lead and lead-particle size data may therefore be desirable.

Air-lead levels along busy streets in smaller towns may not be greatly different than those in street canyons of large cities, notwithstanding a large difference in total traffic volume. Ventilation is profoundly inhibited even in canyons formed by two and three story buildings. Within these city street canyons, air-lead values exceeding 10 μg/m³ were measured while values in the adjacent residential area averaged a few tenths of a μg/m³. These results demonstrate that data obtained from rooftop samplers alone may not adequately reflect actual lead exposures of persons living and working in city street canyons.

5. Acknowledgement

This research was supported by the National Science Foundation through the Research Applied to National Needs program on Environmental Systems and Resources, Grant GI-34813X1.

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DISCUSSION

HARRISON (U.K.)

I would like to point out that one of the published procedures for determination of organic lead in street air involved the passage of the air sample through a membrane filter, assumed to collect particulate lead and then through a scrubber containing iodine monochloride in hydrochloric acid solution. In view of the results presented by Dr. Edwards collection of lead particles passing the filter by the I Cl acid scrubber is probable and this may explain elevated results for levels of organic lead found when using this method, as compared to results determined by other methods.

I have two questions:

1. What experiments were performed to determine blank values for the nitric acid scrubber for lead in reagents and leached from the glass?

2. What was the face velocity of particles at the surface of the membrane filter? Membrane filter efficiences have been shown to be critically dependent upon this velocity.

EDWARDS (U.S.A.)

1. Lead blanks were measured, and the major contribution is the nitric acid reagent blank, about 0.3 X 10^{-9} grams of lead per ml of HNO_3 redistilled twice in quartz. Lead leached from the glass contributes negligibly on a relative basis. Analyses were carried out at lead levels about a factor of ten above the scrubber blanks.

2. Tests with this system were carried out over the face velocity range of about 2 to 50 cm/sec. In this range, no dependence of collection efficiency upon face velocity was observed.

PERRY (U.K.

1. Have you attempted to establish the particle size range of the lead compounds that passed through the filter paper?

2. What is the proportion of this material that exists as organic lead?

EDWARDS (U.S.A.)

No, but this work is underway. One of the difficulties is that in this particle size region, there is no totally satisfactory analytical methodology. A combination of complementary approaches, including electron microscopy and fluorescence, is presently favored.

2. The data presently available do not provide an unambiguous answer to your question. Lead found in the carbon adsorbent may not be only organic in nature, and some organic lead may be eluted from the adsorbent and be caught in the scrubber. At this point, I would agree with use of the term "nonfilterable" to describe lead passing the membrane filter.

PETROLS ADDITIVATED WITH ISOTOPICALLY DIFFERENTIATED LEAD PROPOSAL OF AN EXPERIMENT TO ESTIMATE THE INCIDENCE OF TRAFFIC ON THE ENVIRONMENT POLLUTION BY LEAD - FIRST EXPERIMENTAL RESULTS

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ABSTRACT

When correctly applied the technique used to determine the isotopic composition of lead can be used to monitor the contribution of road traffic to lead pollution in the environment, especially in the atmosphere and in soil, vegetation, food and the human body.

Tests will be carried out in at least two regions of Italy, using petrols containing lead with an isotopic structure which is either identical to or different from that of the lead they currently contain (whether naturally or from some other source).

Analyses of lead samples from major mines have shown that Australian lead (Broken Hill Mine) has a markedly different isotopic composition.

We intend to use this type of lead to prepare anti-knock additives for use in petrols to be marketed in the regions under study. Appropriate sampling should then enable us to determine how far lead pollution is due to exhaust emissions from cars.

Analytical tests on the possible presence of other metals in the atmosphere will provide useful information on the more general problem of atmospheric particulates. The areas selected for this study are Piedmont (Turin and district) and Sardinia (Cagliari City and district); the first was chosen for its high traffic density and high level of industrialization, and the second because it is exceptional in having a high lead content in the soil, which could influence diet. Both these regions are well suited to market distribution of the required type of petrol.

The programme of tests is scheduled to last for three years beginning in spring of 1974. Petrols containing additives of Australian lead will be distributed on the market for a period of 18 months.

Even to-day there still exists differences of opinion on the importance of the different sources of lead pollution, especially as regards motor-car exhaust. In fact, some experts retain the additive-containing petrols as the main source of pollution (1-3), others are not of the same opinion (4-7). Our laboratory tests (8) have enabled us to estimate the amount of lead exhausted in the case of European motor-cars in town traffic conditions. 50-60% of the lead contained in the petrol is exhausted, the remainder is retained by the various parts of the engine (lubricating oil and deposits) and by the exhaust system. Other European Laboratories (9-10) obtained the same results.

The lead contained in the larger particles emitted by the exhaust of the vehicles, falls to the ground at distances of some hundred metres from the roads, whereas the smaller particles are diffused into the atmosphere and are transported even great distances due to the movement of the mass of air (11). The interest in correlating the various sources of lead to environmental pollution is, therefore, evident. Of extreme interest, moreover, is an estimation of the amount of lead exhausted by vehicles absorbed by the human body. The technique of determining the lead isotopic composition, appropriately used, is considered as satisfactorily solving this problem. In fact, several studies (7, 12-22) made to discover the sources of the pollution by means of isotopic analysis, led to the conclusion that such technique can be used successfully providing that the isotopic relation is known in the various sources, that it remains constant therein and that it is sufficiently differentiated in each of them. At present, the mass spectrometry technique enables measurements to be made on quantities of product of less than one microgram with a precision of 0.2-0.3% on the Pb-204 isotope and of 0.1% on the remaining natural Pb-206, Pb-207 and Pb-208 isotopes.

An experiment should be carried out in Italy using lead additive-containing petrol having a differentiated isotopic composition to be employed in large areas having different intensities of traffic. In fact, it is difficult to correlate the lead used as an additive to the petrols to that present in the environment. since the additives normally employed have different and variable isotopic compositions (12). This experiment should lead to:

1) An estimation of the contribution of the vehicles to the lead pollution in the atmosphere and ground in town and country areas.
2) An estimation of the diffusion in the atmosphere at different heights and at various distances from the currents of traffic.
3) A clarification of how the lead is transferred to the vegetation.
4) An estimation of how much of the absorption is inhaled by man.

The experiment can be outlined as follows: the Società Italiana Additivi per Carburanti (SIAC) will use for at least 18 months only Australian lead (Broken Hill mine). In fact, our analyses on metallic lead samples obtained from the mines that normally supply Europe, have shown that the Australian Pb possesses a sufficiently differentiated isotopic composition (Table I)

Table I

ISOTOPIC RATIOS OF LEAD SAMPLES USUALLY SUPPLIED TO THE ITALIAN MARKET

Origin	$\frac{\text{Pb } 206}{\text{Pb } 204}$	$\frac{\text{Pb } 207}{\text{Pb } 204}$	$\frac{\text{Pb } 208}{\text{Pb } 204}$	$\frac{\text{Pb } 206}{\text{Pb } 207}$	$\frac{\text{Pb } 208}{\text{Pb } 207}$
Australia (Broken Hill mine)					
Sample arrived at Bussi 4.11.72	15,7	15,1	35,1	1,04	2,32
Sample arrived at Bussi 19.2.73	15,7	15,1	35,1	1,04	2,32
Sample arrived at Bussi 21.9.73	15,7	15,1	35,1	1,04	2,32
South Africa	17,8	15,4	37,4	1,16	2,43
Cerro de Pasco, Peru	18,0	15,0	37,6	1,20	2,51
Mexico	15,9-19,5	13,2-16,1	32,6-40,6	1,21	2,47-2,52
Canada	18,2	15,7	38,6	1,16	2,46
Southern Italy	17,4-18,3	15,2-15,9	37,9-39,1	1,15	2,48

In certain areas, only petrol containing Australian lead will be distributed. Before this petrol will be placed on the market, the lead isotopic composition will be determined in these areas on all types of samples which will later be analysed. Once the Australian lead additive-containing petrol is introduced on the market, the same determinations will be repeated at intervals in order to be able to follow the variations in the isotopic composition of the lead. Once the production of anti-knock additives having a base of Australian lead have been concluded, a new variation will be made in the isotopic composition of the lead in the same types of samples. During the experiment, a control will be effected on the lead imported into Italy for any other use.

It is clear from the foregoing that the experiment is both vast and complex and necessary in order to have a significant analysis that can solve such an important problem.

Italy is particularly suitable for such an experiment for the following reasons:

- its refining capacity exceeds its consumption and therefore exports part of the petrol produced
- a high percentage of the alkyl lead used as an additive is produced by only one firm (SIAC)
- the importation of lead, no matter how used, is subject to government authorisation; it is, therefore, possible to control the isotopic composition of all the lead imported
- there is a high traffic intensity.

Table II

ITALIAN PETROLIFEROUS SITUATION IN 1972

	tons x 100
Unrefined petrol processed by the refineries that produce petrol	110.329
Petrol produced	12.707
Petrol consumed	10.400

Table II gives the total quantity of unrefined petrol processed in Italy, the amount of petrol produced and the quantity of petrol consumed in the year 1972.

TABLE III

ANNUAL CONSUMPTION OF LEAD IN ITALY IN 1971

	tons x 1000	%
METALLIC STATE		
Semi-processed	56,5	27,2
Electric cables	29,5	14,0
Accumulators	56,0	27,0
Alloys	6,0	3,0
Total metallic state	148,0	71,2
CHEMICAL COMPONENTS		
Oxides	35,6	17,1
Anti-knock additives	15,3	7,3
Other chemicals	3,3	1,6
Sundry	5,8	2,8
Total chemical components	60,0	28,8
Total lead consumed	208,0	100,0

Table III relates to the consumption of lead during 1971 divided according to use.

TABLE IV

CIRCULATION IN ITALY IN 1972

Motor-cars	12.484.313
Lorries	995.591
Buses	36.150
Total	13.516.054
Density (n° inhabitants x vehicles)	4.0

Table IV indicates the circulation for the year 1972 divided between petrol driven vehicles and diesel driven vehicles.

Since it is not possible, for obvious reasons, to effect the experiment all over Italy, it was decided to choose the most suitable regions. Selection was made as follows:

- possibility of the complete supply of petrol by the refineries located in the region or adjacent regions
- present vast use of alkyl lead produced by SIAC in these refineries so as to limit exchanges with other suppliers
- availability of a city having a high traffic intensity and a high industrial level.

An appropriate study carried out showed that Piedmont (especially Turin and province) offered interesting prospects for the work to be carried out. In fact, the area satisfies the above requirements and in Turin, for some time now, an efficient network of centres for the recording of atmospheric conditions (Fiat centres) has been in operation. Sardinia (Cagliari and province) was chosen as a comparison for the following reasons:

- excess of refined petrol
- SIAC produced alkyl lead (>90%)
- the region is completely isolated
- the high lead concentration in the ground offered the possibility of being able to evidence both the contribution due to the traffic and that due to natural lead in the environment and in man.

The above experiment should take about 3 years. We have started an experimental investigation to determine the present level of lead pollution especially for the determination of the lead isotopic composition present in the various sample environments. This investigation is at present limited to Piedmont (Turin and province) and to the following aspects:

- atmosphere involved
- washout

- human body (blood and urine)

Atmosphere involved

Samples were taken in Turin and analyses were made of the isotopic composition by means of mass spectrometry and of the concentration by means of atomic absorption. At Turin, and for comparison at Ispra which can be considered as a semi-rural area, samples were also taken by means of the Andersen particle fractionator which enables the dust to be divided into fractions of different granulometry. On the dust thus fractioned, also semiquantitative determinations of other metals are made in addition to the isotopic and quantitative analyses of lead. The first results obtained are given in Table V.

Table V

Isotopic rations in the lead present in the atmosphere of Turin

Sample		Place	Pb Conc. $\mu g/m^3$	$\frac{Pb\ 206}{Pb\ 207}$	$\frac{Pb\ 208}{Pb\ 207}$	$\frac{Pb\ 206}{Pb\ 204}$
No	Date					
1	28.2.74	C. Novara	8.1	1.21	2.51	19.58
2	28.3.74	P. Carducci	6.2	1.22	2.49	19.83
3	2.3.74	P. Statuto	5.0	1.22	2.46	17.80
4	2.3.74	C. Novara	1.5	1.20	2.52	18.83
5	1.3.74	P. Carducci	5.5	1.22	2.48	19.84
6	20.3.74	P. Statuto	5.1	1.22	2.46	18.97
7	20.3.74	P. Carducci	3.2	1.20	2.49	18.46
8	20.3.74	C. Novara	4.0	1.21	2.54	19.43
9	24.3.74	P. Carducci	6.5	1.18	2.49	21.70

Washout

The experiment of radioactive fallout, that is, of the radionuclides produced and dispersed all over the world following nuclear explosions, has demonstrated that the non-gaseous substances emitted into the atmosphere return in time and different mechanisms on the surfaces of the world. Generally, in the removal of the substances tied to the solid particles dispersed in the atmosphere, the action of the precipitations greatly prevails on all the other causes. Such removal occurs through two main mechanisms: The first, called rainout (or snowout) consists in the incorporation of the particles by the drops of rain in the formation of clouds; the second, called washout consists in the elimination of the particles by the drops that fall. Since the greater part of these remarks in this field concern the radionuclides of the fallout, released at a high altitude, a lot of information is available on the global effect of the mechanisms of rainout + washout but there is very little information on the washout effect alont. In view of the fact that the lead, with the particular isotopic relations of this experiment, will be released into the atmosphere at ground level, it will, therefore, be possible to determine the entity of the washout effect for lead by measuring the concentration in air and in rainwater. This phenomenon has already been observed in New York (23, 24) for the global lead and other metals. In Turin and at Ispra we have started to observe the quantity of Pb globally deposited, in precipitation essence and with single showers of rain; in paralles, daily determinations are made of the Pb concentration in the atmosphere by collecting the dust of some hundred cu.m of air on filters.

Human body

The final aim of the investigation is the estimation of the contribution made by the traffic to the lead absorption by the human body. As far as we know, there are only two jobs (7, 22) that have faced this problem by means of isotopic analyses. Due to the different metabolic models used, different results were obtained, especially on the time necessary to observe a variation of the isotopic composition in the blood, once that of the environment has been modified. Rabinowtz and coll. (7) determined the variation of the lead isotopic composition in the blood caused by the ingestion of food marked with ^{204}Pb; consequently, the human blood in a relatively short time (some weeks) is affected by the variation of the isotopic composition of the diet. Although limited to one person, it was demonstrated that the contribution of the diet is approximately 50%.

The research proposed by us is complementary to this work in that it refers, above all, to the contribution due to inhalation and will have, in addition, the advantage of having available a practically unlimited number of subjects.

Determinations of the isotopic composition and concentration are being made on a series of blood and urine specimens taken by the Institutes of Hygiene in the city and provinces of Turin, in Milan and Ispra.

The present value of the isotopic relations in the human body and the reproducibility in time of such measurements will also be determined.

Table VI

Isotopic ratios of 4 blood samples from Ispra and Turin

Sample No	City	PbConc. µg\100ml	$\frac{Pb206}{Pb207}$	$\frac{Pb208}{Pb207}$	$\frac{Pb206}{Pb204}$
1	Ispra	36	1.18	2.45	18.91
2	Ispra	26	1.19	2.45	19.04
3	Turin	34	1.19	2.43	19.53
4	Turin	50	1.18	2.46	17.92

In this way, it is wished to ensure that possible variations due to the additive-containing petrol with Australian lead are not hidden by fluctuations to be attributed to other causes. The first results are given in Table VI.

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DISCUSSION

BOUQUIAUX (Belgium)

What time is required for the isotopic change in lead in gasoline additives to have a significant effect on the isotopic composition of lead in human blood?

FACCHETTI (JRC - Ispra)

I should like to refer to the experimental results of Wetherill et al, which although based on a small number of subjects, I consider to be more reliable than forecasts obtained from metabolic models. With the use of a Pb 204 labelled diet a significant response was obtained after some two weeks. Assuming, still on the basis of the Wetherill study, that the incidence due to inhalation is approximately 30-40% of the total blood lead, a measurable change in the isotopic composition of blood lead ought to be observed after a few months since the gasolines will have lead additives which have an isotopic composition differing by 10-15% from that presently in use.

As stated earlier, these gasolines are to be used in Italy for a period of at least two years.

WETHERILL (U.S.A.)

1. Will this experiment change the isotopic composition of lead in gasoline over all of Italy of just in the two regions under study?

2. What will be the time required to change the isotopic composition of gasoline?

FACCHETTI (JRC - Ispra)

1. SIAC, who supply 75-80% of the Italian market, are only going to use Australian lead. At present they supply over 90% of the gasoline in the two regions in question (Piedmont and Sardinia). Agreements have been made to the effect that in these two regions and neighbouring districts exclusively Australian lead will be used, while the lead distributed by other suppliers (∿20-25% of the total) will be used in regions far from those under study.

2. The time required in the SIAC plants for stoppage, clean-up and restart is estimated to be around two weeks. The production of a sufficient quantity of lead alkyls and distribution to the refineries should take a further two months. This would give enough time to use up old stocks. Furthermore, the refineries have agreed not to use any additive left over. Thus, from technical aspects, it will take altogether some 4 months before the regions under study and their neighbouring districts are actually being supplied exclusively with gasolines with Australian lead additives.

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UMWELTMESSUNGEN
ENVIRONMENTAL MEASUREMENTS
MESURES DANS L'ENVIRONNEMENT
MISURE AMBIENTALI
METINGEN IN HET MILIEU

Vorsitzender - Chairman - Président - Presidente - Voorzitter

S. CERQUIGLINI-MONTERIOLO
(Italia)

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APPLICATION DU COMPTEUR COULTER A L'EVALUATION DE LA MESURE DE LA POLLUTION ATMOSPHERIQUE PAR LA MESURE DES PARTICULES SOLIDES EN SUSPENSION DANS L'ATMOSPHERE

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RESUME

Une méthode se basant sur l'utilisation du compteur Coulter est proposée pour mesurer le nombre de particules dans l'atmosphère en fonction de leur dimension.

Des particules atmosphériques sont prélevées sur un filtre en nitrate de cellulose puis sont mises en suspension par dissolution du filtre dans un liquide organique rendu préalablement conducteur. Connaissant la dilution effectuée et la quantité d'air prélevé on peut calculer la courbe de distribution des particules atmosphériques par le compteur Coulter.

Le compteur Coulter est basé sur le principe suivant: un tube en verre ayant une ouverture calibrée est plongé dans un liquide conducteur. De part et d'autre de cette ouverture, se trouve une électrode immergée. On fait circuler le liquide avec les particules en travers de l'ouverture du tube; chaque passage de particule fait varier la résistance entre les deux électrodes et produit une impulsion de tension dont l'amplitude est proportionnelle au volume de la particule. Moyennant des discriminations électroniques, on peut alors faire aisément le comptage suivant diverses dimensions et obtenir la courbe de distribution des particules en suspension.

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Nos recherches ont porté sur l'efficacité de différents solvants en vue de réaliser un solvant organique conducteur donnant les résultats les plus stables et les plus reproductibles.

Nous avons effectué par cette méthode une étude comparative de la pollution atmosphérique entre un site rural et un site urbain.

Nous soulignons la facilité, la rapidité, la reproductibilité de cette méthode, les dimensions des particules mesurées pouvant aller de 200 à 0,6 μ.

ABSTRACT

A method based on the use of the Coulter counter is proposed to measure the number of particles present in the atmosphere by size.

Atmospheric particles are collected on a cellulose nitrate filter and placed in suspension by dissolving the filter in an organic liquid which has first been made conductive. From the known degree of dilution achieved and volume of air samples, it is possible to calculate the distribution curve for the atmospheric particles by means of the Coulter counter.

The Coulter counter is based on the following principle: a glass tube with a calibrated aperture is placed in a conducting liquid. To each side of this aperture there is an electrode immersed in the liquid. The liquid containing the particles is passed through the tube aperture; each particle passing through causes the resistance between the two electrodes to vary,

producing a voltage pulse, the amplitude of which is proportional to the volume of the particle. By means of electronic discriminations it is then easy to count the suspended particles according to size and plot their distribution curve.

Our experiments concentrated on testing the efficacity of various solvents with a view to finding a conductive organic solvent which would yield the most stable and most reproducible results.

Using this method we carried out a comparative study of air pollution in a rural and an urban location.

We should like to emphasize that this method is easy, fast and reproducible, and can measure particles of 200 to 0.6 μ in size.

1. Introduction.

Les problèmes posés par la détermination de la distribution granulométrique des particules solides dans l'air sont de deux ordres: d'une part le prélèvement de ces particules en suspension dans l'air, et d'autre part le comptage des particules prélevées et leur répartition en fonction de leur dimension.

D'une manière générale, le prélèvement des particules peut être incomplet soit pour les petites particules dans le cas de l'impinger et de la sédimentation (1,2) soit pour les grosses particules dans le cas de la précipitation thermique. Nous avons utilisé des membranes filtrantes dont la dimension des pores est connue, ceci permet de fixer avec certitude la limite inférieure de la dimension des particules prélevées.

Pour le comptage des particules nous proposons la mise en suspension des particules dans un liquide organique par dissolution du filtre et leur comptage à l'aide d'un compteur Coulter ZB, ce compteur permet de compter et de classer rapidement un grand nombre de particules. La dimension des particules se situant dans le cas qui nous préoccupe entre 0,6μ et 40μ.

2. Description de la méthode de prélèvement et d'analyse.

2.1. Prélèvement des particules.

L'air est aspiré par une pompe à vide sur la membrane filtrante à l'aide du dispositif décrit par la figure 1.

La pompe à vide (Becher VT.3) assure un débit nominal de l'ordre de 3m^3/h. Elle est pourvue d'un vacuomètre et d'une soupape de régulation de vide qui permet un règlage continu du débit entre 0 et 3m3/h.

On utilise un support de filtre Millipore en P.V.C. d'un diamètre de 50mm. Un joint thorique assure une étanchéité parfaite. Un capuchon de protection placé au sommet du porte-filtre protège efficacement la membrane de la pluie et de retombées diverses.

Les membranes filtrantes sont des membranes Sartorius type 11302 en nitrate de cellulose. Elles sont caractérisées par une structure régulière et spongieuse avec des grandeurs de pores bien définies. Nous avons utilisé des membranes de porosité 1,2μ. Nous notons que pour la filtration des gaz, le degré d'efficacité des membranes filtrantes est considérablement augmenté par des forces électrostatiques. C'est ainsi que la membrane utilisée possède un diamètre de pores de 1,2μ mais retient également des particules dont le diamètre est de l'ordre de 0,4μ.

La mesure du débit est assurée par un rotamètre (Rota L 63/2400) inséré entre la tête de prélèvement et la pompe à vide. Ce débimètre permet l'évaluation de débits compris entre 0 et 2,4m3/h.

2.2. Le compteur Coulter.

Le compteur Coulter permet de compter électroniquement les particules suivant leur dimension. Son principe a déjà été décrit longuement dans la littérature et nous renvoyons aux différents articles s'y rapportant.

Rappelons toutefois que les particules doivent être mises en suspension dans un liquide conducteur (3, 4, 5, 7).

Le compteur utilisé est le modèle ZB; il permet de situer les seuils inférieurs et supérieurs des dimensions des particules, ou de faire des comptages du nombre des particules au-dessus d'un diamètre donné (nombre cumulatif). Ce compteur a été préalablement étalonné à l'aide de particules sphériques de latex de dimensions homéodisperses de 5,02μ et 16μ.

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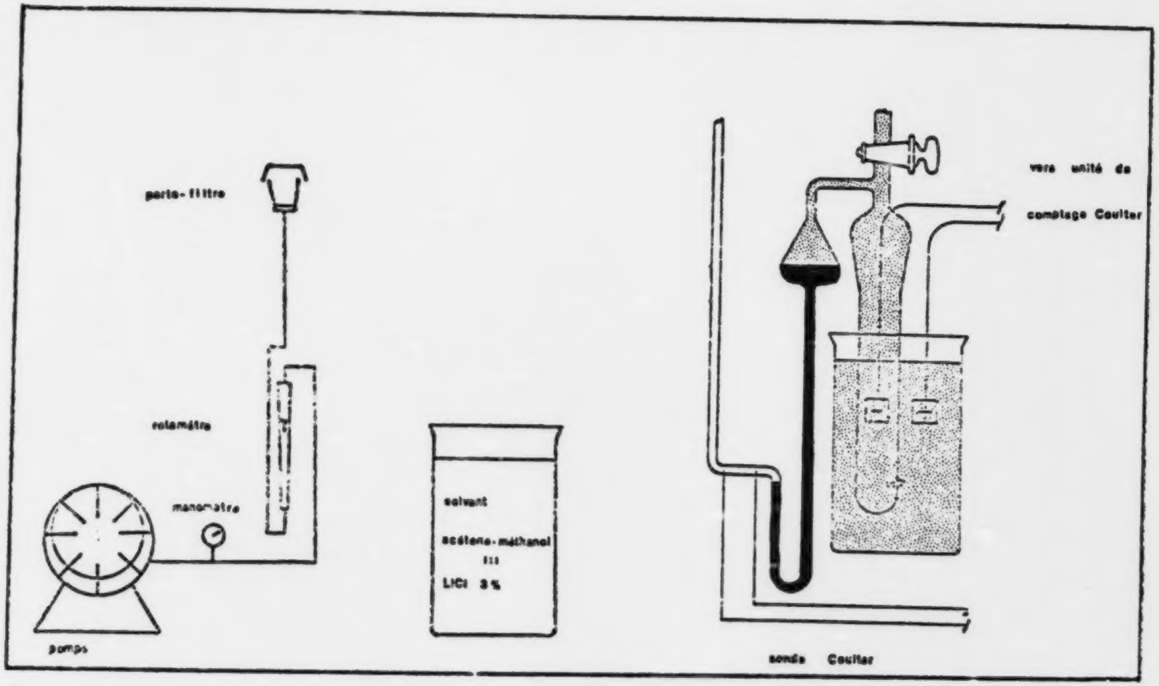

Figure 1: Mode de prélèvement et d'analyse des particules solides en suspension dans l'atmosphere et traitement du filtre pour le comptage au compteur Coulter.

Les dimensions des particules comptées sont exprimées en diamètre d'une sphère de volume équivalent, étant donné que la réponse du compteur est proportionnelle au volume des particules, quelle que soit leur forme.

2.3. Traitement du filtre en vue du comptage des particules.

Après un prélèvement de 24heures (soit environ 35m^3 d'air aspiré), les particules sont détachées de la membrane par mise en solution de celle-ci dans un solvant organique composé d'un mélange 1:1 acétone-méthanol. Ce solvant a été filtré sous pression sur une membrane en cellulose régénérée de 0,2µde porosité. Ce solvant a été rendu, au préalable, conducteur par l'addition de 3% de chlorure de lithium. On dissout généralement un quart de membrane dans 200cm^3 de solution. Cette solution est directement prête pour le comptage . La possibilité de dissoudre le filtre permet d'écarter les inconvénients de la mise en suspension des particules par ultra-sons (7). Le comptage des poussières défini comme le nombre de particules contenu dans un volume déterminé de solutionest réalisé après le passage de 0,5 ml de la suspension du travers du tube a orifice Coulter de 100µ.
L'utilisation d'un tel tube permet de compter des particules dont le diamètre se situe entre 1,6µ et 40µ.
La concentration particulaire des échantillons pour les diverses dimensions est évaluée à partir de l'équation suivante:

$$(p) = \frac{(n - n_0)\ Vd}{Vm \cdot Va} \qquad (1)$$

(p) = concentration des poussières en nombre de particules par m^3 d'air.
n = nombre moyen de particules dans le solvant.
n0 = nombre moyen de particules dans la solution d'électrolyte ayant dissous une membrane filtrante vierge (blanc).
Vd = volume de solution dans lequel est dissous la membrane filtrante chargée.
Vm = volume du solvant sur lequel s'effectue le comptage.
Va = volume d'air aspiré.

3. Validité de la méthode et résultats obtenus.

La principale difficulté fut le choix d'un solvant organique compatible d'une part avec le comptage au Coulter c'est-à-dire conducteur et d'autre part dissolvant parfaitement la membrane afin de mettre les particules en suspension. Nous avons vérifié la validité de chacunes des étapes du comportement du solvant seul, de la mise en solution d'un filtre vierge, la mise en solution d'un filtre chargé, la statistique du comptage, la reproductibilité dans l'échantillonnage.
D'une manière générale, les résultats sont exprimés en nombre cumulatif de particules pour une dimension de particules donnée. Les comptages se font sur 0,5cm^3 de solution (Vm).
Le tableau 1 donne pour deux dimensions de particules le nombre des particules restant après que le solvant ait été filtré.

Tableau 1.

Dimension des particules.	n	déviation standart.	Coef. de variation.
2,1 µ	60	12	0,2
10,6 µ	2,4	0,4	0,18

Lorsqu'on dissout 1/8 de filtre vierge dans 50cm3 de solvant on obtient alors les taux de comptage suivants (moyenne sur 20 comptages):

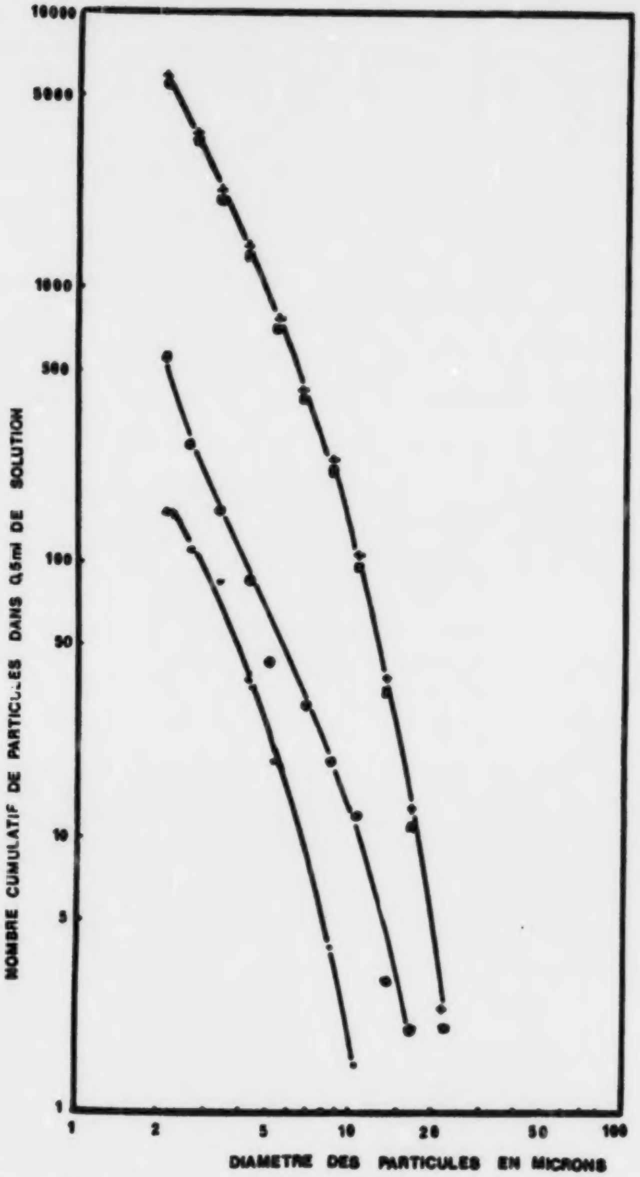

Figure 2: Représentation graphique de comptages au compteur Coulter pour
- ● solvant seul
- ○ solvant avec 1/8 de filtre dans 50 cm^3, (blanc)
- + 1/8 de filtre chargé dissous dans $50cm^3$ de solvant.
- □ différence entre le filtre chargé et le blanc.

Tableau 2.

Dimensions des particules	n	Déviation Standart	Coefficient de variation.
2,1 μ	711	138	0,194
10,6 μ	13	4,5	0,34

Ces résultats montrent que la dissolution du filtre apporte malgré tout des impuretés.

Ces résultats pourraient être quelque peu améliorés par l'utilisation d'acétone pure mais d'une part celle-ci s'évapore rapidement ce qui donnera une imprécision sur le volume et d'autre part on est confronté a des problèmes techniques tel la déterioration rapide de certains éléments de l'appareillage lors d'une utilisation intensive (graissage des robinets, tuyaux en P.V.C.).

Lorsqu'on effectue des comptages à différents niveaux électroniques (c'est-à-dire différents diamètres) sur un filtre chargé, la reproductibilité des comptages est donnée par le tableau 3: les calculs ont été effectués sur 50 comptages.

Tableau 3.

Dimension des particules.	n	Déviation Standart.	Coefficient de variation.
2,1 μ	12.310	266	0,02
4,2 μ	71,9	8	0,11
22,4 μ	5,4	2,5	0,46

Ayant résolu les problèmes se rapportant au comptage même on peut alors se poser la question de la reproductibilité de la mesure lorsque différentes parties du filtre sont utilisées (1/8 de filtre est analysé chaque fois). D'autres part, on a vérifié la validité des résultats lorsque l'on effectue des prélèvements simultanés à l'aide de deux systèmes de prélèvements placés au même endroit.

Les résultats obtenus sont résumés dans le tableau 4 où l'on a chaque fois utilisé 4 x 1/8 de filtre dissous dans 50cm^3 de solution et ensuite les résultats ont été exprimés en nombre de particules par m3 en se basant sur la relation(1).Les calculs se rapportent à des particules de 2,1 μ

Tableau 4.

	Prélèvements 1			Prélèvements 2		
Echantillons.	n	s	CV	n	s	cv
1	10750	245	0,02	11366	121	0,01
2	11210	223	0,02	11281	195	0,017
3	10491	179	0,017	10866	122	0,01
4	10726	204	0,02	11121	160	0,014
moyenne	10797	339	0,03	11158	243	0,02
nbre m3 d'air aspiré	38,189 m^3			39,205 m^3		
nbre part. par m3	209.400 part./m^3			213.177 part./m^3		

La figure II donne un exemple de courbe de distribution des particules dans le solvant pur, dans le solvant plus un filtre vierge dissous,

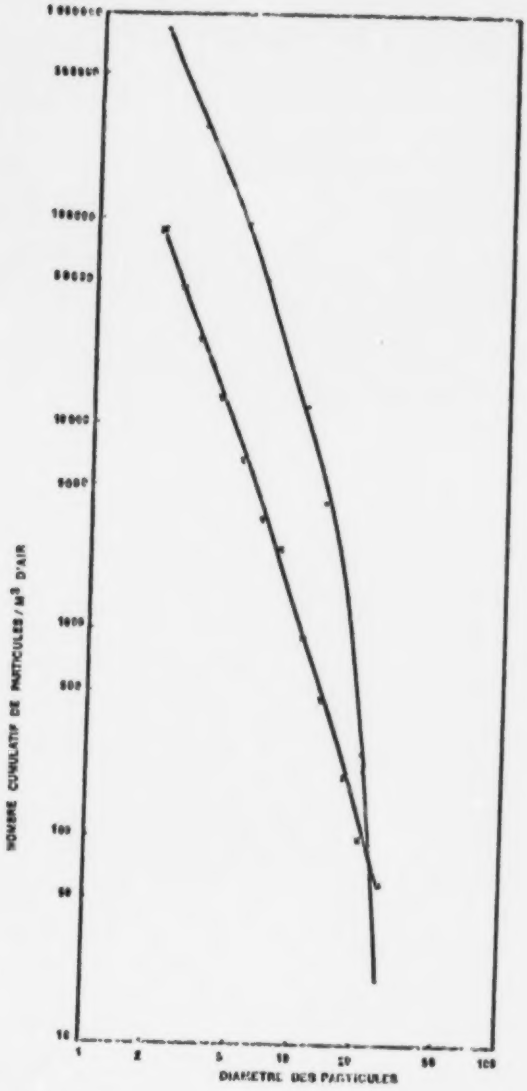

Figure 3: Exemples de représentation graphique du nombre cumulatif de particules par m^3 d'air en fonction de leur diamètre.

× Bruxelles le 1 avril 1973

● Bruxelles le 21 novembre 1973

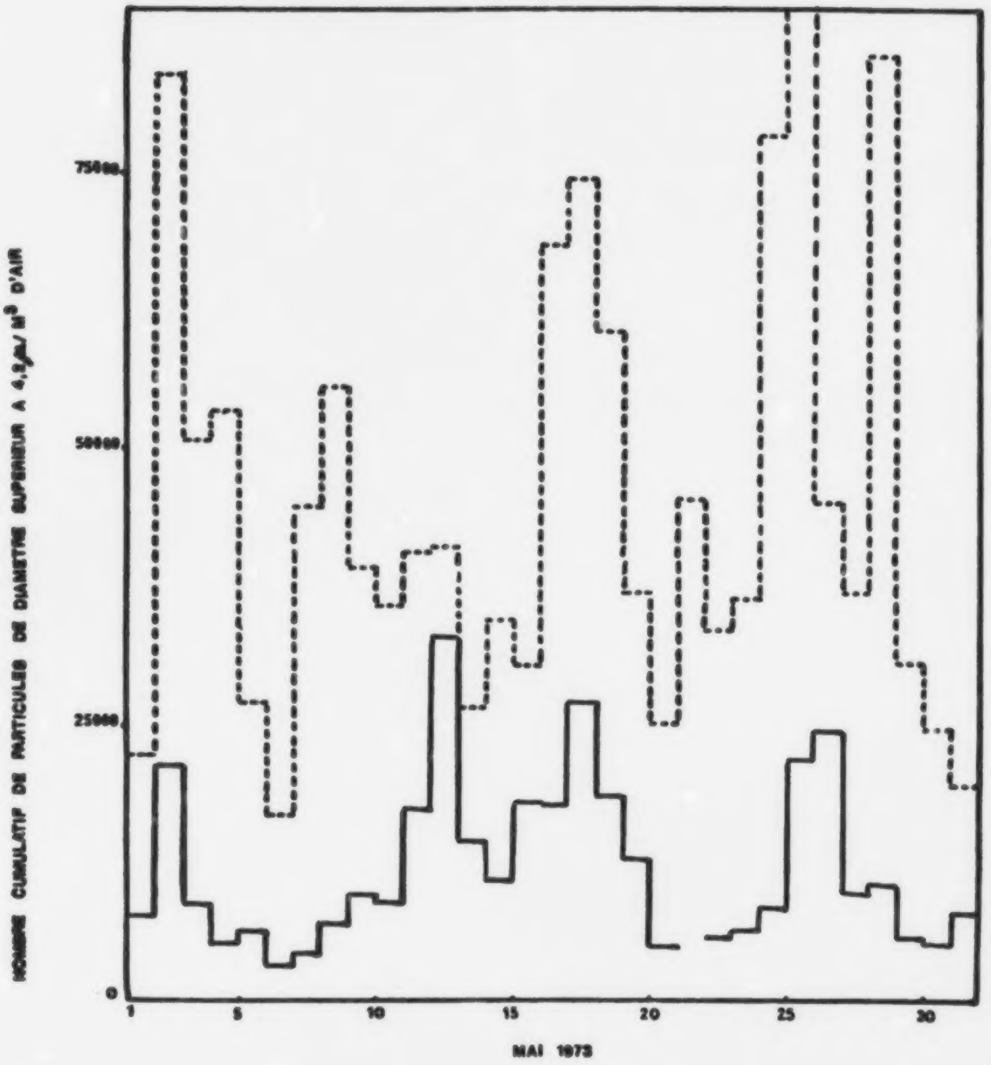

Figure 4: Evolution du nombre cumulatif du nombre de particules de diamètre supérieur à 4,2 par m^3 d'air au cours du mois de mai 1973 pour Bruxelles (- - -) et Dourbes (——).

ainsi que pour un filtre chargé, la différence entre un filtre chargé et le blanc. Les comptages ont été effectués sur 0,5cm^3 de solution.
La figure III donne un exemple de courbe de distribution obtenue. Enfin on a montré que l'on peut appliquer sur les prélèvements atmosphérique cette méthode pour suivre l'évolution de la pollution atmosphérique en particules pour une dimension de particules bien définies.
La figure IV donne un exemple de mesure de l'évolution du nombre total de particules de 4,2μ pendant un mois et ce en comparant un site urbain (Bruxelles) et un site rural (Dourbes).

4. Conclusion.

On peut dire que cette méthode se caractérise par sa simplicité, par sa rapidité et par sa facilité de manipulation. Elle permet des comptages rapides et statistiquement valables.
Ces différents critères font qu'elle peut aisément être adaptée sur une grande échelle à une étude de la pollution atmosphérique par les particules solides.

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DISCUSSION

PICHE (Canada)

Quelles sont les raisons qui vous empêchent d'installer votre appareil compteur sur le terrain même, de façon permanente ou temporaire (roulotte) afin d'éviter les difficultés inhérentes à la méthode que vous utilisez qui est sujette à toutes les interventions du solvant dans lequel il vous faut éventuellement éluer les prélèvements rapportés au laboratoire?

KUMMER (Belgique)

Le compteur COULTER se prête mal à une utilisation sur le terrain ou en automatique notamment à cause d'une possibilité de bouchage du tube à orifice de la sonde Coulter.

Ensuite le but de l'étude était de faire des mesures de la pollution atmosphérique par les particules, cette étude est notamment à mettre en relation avec celle effectuée par le Dr. Dams, et par conséquent, nous n'étions pas intéressés de disposer d'appareils automatiques.

Il faut aussi tenir compte du fait que le coût des installations automatiques placées en divers sites est nettement plus élevé que si l'on dispose d'une seule installation au laboratoire qui analyse les échantillons arrivant des différents sites. D'autre part, je tiens à signaler que nous n'avons pas observé de différence notable entre un échantillon traité directement au laboratoire immédiatement après le prélèvement et un filtre du même prélèvement qui a été au préalable envoyé par la poste.

DUPUIS (France)

Avez-vous fait des prélèvements à l'aide d'appareils de prélèvements individuels? Dans l'affirmative, les résultats obtenus concordent-ils avec les résultats théoriques calculés à partir des comptages faits avec des appareils à postes fixes?

KUMMER (Belgique)

L'appareillage de prélèvement dont on dispose se prête assez mal à des prélèvements individuels, quoi que l'on pourrait envisager une adaptation à cet effet.

Seuls des prélèvements à des postes fixes ont été effectués avec cet appareillage.

MOREAU (France)

La technique proposée par l'auteur recueille à la fois les particules de nature "physique" et les autres "biologiques" c'est à dire, dans les tailles retenues: bactéries spores de champignons, grains de pollen. La technique mettant les filtres en dissolution - et utilisation des ultrasons - va séparer en éléments isolés ces particules biologiques.- elle risque donc d'être faussée lors de la multiplication de ces microorganismes (fonction des conditions écologiques ...)

En effet, les celles bactériennes sont rarement vehiculées seules dans l'air mais seraient absorbées (cf. récentes journées ASPEC à l'Institue Pasteur: biocontamination en salles d'opération et milieu hospitalier) sur des particules inertes > à 6 µ ou = à 2 µ selon leur structure de paroi (c'est à dire selon leur réaction de Gram). Quant aux spores de champignons, selon les cas, elles "voyagent" seules ou groupées mais il y a des très fortes fluctuations journalières (certaines spores libérées à 12 h d'autres à 24 h etc ...) selon que l'air est sec ou humide, calme ou agité, etc ...

Comme certains de ces organismes sont pathogènes, que certaines espèces fongiques sont allergènes ... on ne peut guère ne pas en tenir compte dans une enquête générale.

KUMMER (Belgique)

1. Etant donné que nous mettons des filtres sur lesquels ont été faits les prélèvements en solution, nous écartons certains problèmes tels que la désagrégation des particules comme c'est le cas lors de l'utilisation des ultra-sons.

2. Dans cette mesure on tient compte de la dimension globale de la particule (même s'il y a des particules qui restent absorbées sur celle-ci). C'est d'ailleurs cette dimension globale qui est importante lorsqu'on examine les problèmes de pénétration des particules dans les voies respiratoires.

3. Etant donné que les prélèvements se font à l'extérieur, les quantités de particules d'origine biologique sont certainement négligeables à côté des particules d'origine minérale.

GOOTJES (Pays-Bas)

1. Quel est l'intérêt pratique de la méthode hors laboratoire?

2. Comment définit-on la poussière? Il est de peu d'intérêt de parler des méthodes si l'on ne connait pas les substances qui la composent.

KUMMER (Belgique)

L'intérêt pratique de cette étude réside dans le fait qu'il est certainement plus intéressant de connaître la distribution granulométrique des particules en suspension dans l'atmosphère et par conséquent de connaître le nombre des particules susceptibles de pénétrer dans les voies respiratoires, que d'avoir une donnée élémentaire qui est le poids total des particules en suspension dans l'air.

Pour ce qui est de la définition de la poussière du point de vue composition, cette étude est à mettre en relation avec celle notamment effectuée par le Dr. Dams pour la composition minerale des particules ou encore les mesures des composés organiques proposées par divers auteurs.

ULTRASPURENANALYSE ORGANISCHER SCHADSTOFFE IN DER LUFT MITTELTS DER SOGENANNTEN THERMOGRADIENTTECHNIK

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KURZFASSUNG

Es wird eine Methode vorgestellt, die einen qualitativen und quantitativen Nachweis organischer Luftverunreinigungen im Ultraspurenbereich erlaubt. Ihr ökotoxikologischer Wert wird einmal darin gesehen, dass Schadstoffe bereits in Konzentrationen nachgewiesen werden können, die isoliert betrachtet vielfach wohl als atoxisch gelten dürfen, in ihrer Summe durch Additions- oder Potenzierungseffekte aber umweltmedizinisch relevant werden. Periodisch zur Qualitätskontrolle der Atmosphäre eingesetzt ergeben sich hier ausserdem Ansatzpunkte für ökopräventive Massnahmen, indem neu immittierte Schadstoffe frühzeitig erkannt und rechtzeitig entsprechende Gegenmassnahmen eingeleitet werden können.

ABSTRACT

A method is presented which enables organic air pollution in the ultra-trace range to be detected qualitatively and quantitatively. One aspect of its value for the study of environmental pollution is that pollutants can be detected in concentrations which, taken in isolation, may well often be considered atoxic but which, in combination, have a bearing on environmental health

as a result of their cumulative or potentiating effects. Another is that, when used for periodic atmospheric quality checks, this method provides information on which environmental protection measures can be based, since it enables newly immitted pollutants to be detected early and appropriate counter-measures to be taken in time.

Im vergangenen Jahrzehnt ist auf Teilgebieten der Ökotoxikologie ein großer Wissensfundus erarbeitet worden. Andere Sektoren, insbesondere die atmosphärische Verunreinigung mit organischen Schadstoffen blieben bis heute dagegen weitgehend unerforscht. Wenngleich davon ausgegangen werden darf, daß jede einzelne dieser Substanzen für sich unseren Lebensraum meist nur in subtoxischen Konzentrationen kontaminieren, so gewinnen sie doch dadurch an umweltmedizinischer Bedeutung, daß sich nach neueren Erkenntnissen zahlreiche Agentien in ihrer biologischen Wirkung zu addieren oder zu potenzieren vermögen. Einer unter diesen Aspekten notwendig werdenden routinemäßigen Erfassung der auch in Ultraspurenkonzentrationen vorhandenen Luftverunreinigungen war bisher aber durch die Nachweisgrenzen der analytischen Methoden eine deutliche Grenze gesetzt.

Art und Vielzahl der nachzuweisenden organischen Stoffe lassen zur qualitativen wie quantitativen Identifizierung der Komponenten einen Einsatz der Kombination Gaschromatographie-Massenspektrometrie als Methode der Wahl erscheinen. Die zuvor genannten Gründe machen jedoch eine vorhergehende Anreicherung der Komponenten unumgänglich, auch dann, wenn statt des Massenspektrometers relativ empfindlichere Detektoren verwendet werden. Zur Anreicherung der Komponenten verwenden wir ein sogenanntes Thermogradientrohr, wie es zuerst von Kaiser [1] vorgeschlagen wurde. Dabei werden ca. 2 l der Luftprobe durch das über eine Doppelwandung gekühlte, mit einem Sorptionsmaterial gefüllte Thermogradientrohr gesaugt. Anschließend werden die retinierten Komponenten unter Erwärmung des Thermogradientrohres mit dem Trägergasstrom auf die gekühlte Trennsäule eines Gaschromatographen überführt. Unter Anwendung eines linearen Temperaturprogramms wird der Ofenraum des Gaschromatographen von -150 °C auf +200 °C aufgeheizt. Die gaschromatographisch getrennten Komponenten werden dann,

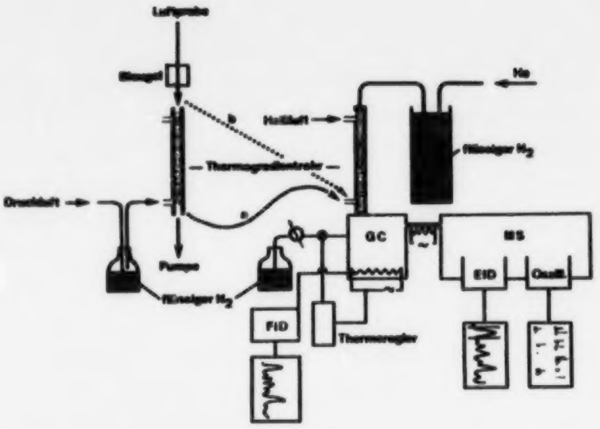

Abb. 1. Schematische Darstellung des apparativen Aufbaues bei der Thermogradient- Gaschromatographie-Massenspektrometrie-Analyse von Luftproben.

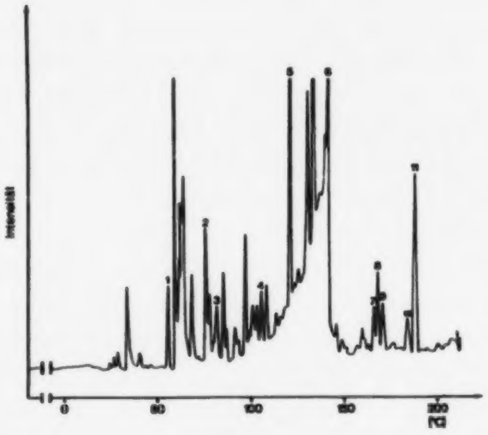

Abb. 2. Verwendung von 10% Dexsil GC 300 auf Chromosorb G/AW-DNCS, 80 - 100 mesh als Sorptionsmittel im Thermogradientrohr. 1 Methanol; 2 Aceton; 3 Pentadien; 4 Hexan; 5 Benzol; 6 Toluol; 7 - 9 o, m, p-Xylol; 10 - 11 Trimethylbenzole.

wie von uns andernorts [2] beschrieben, wahlweise mit einem FID bzw. mit dem EID eines Massenspektrometers nachgewiesen. Die qualitative Identifizierung der Komponenten erfolgt durch die mit einem Galvano-m-Schreiber gleichzeitig aufgenommenen Massenspektren. Den Aufbau der gesamten von uns verwendeten Gerätekombination veranschaulicht schematisch Abb. 1.

Mit dieser Meßanordnung konnten wir in "normaler" Raumluft aus der Vielzahl der tatsächlich vorhandenen Fraktionen bisher etwa 30 organische Komponenten ähnlicher Konzentrationen abtrennen und identifizieren (Abb. 2 und Tab. 1). Ähnlich günstige Resultate wurden inzwischen mit einer im Prinzip unserem Verfahren entsprechenden Gerätekombination von einer anderen westdeutschen Arbeitsgruppe [3] mitgeteilt.

Im Falle der Abb. 2 diente als Füllung des Thermogradientrohres Dexil 300 GC auf Chromosorb. Verwendet man stattdessen Porapak Q als Sorptionsmaterial, so liefert die gleiche Raumluftprobe ein völlig anderes Chromatogramm. Wie Abb. 3 zeigt, werden mit diesem Sorptionsmaterial wesentlich weniger Komponenten retiniert. Andererseits werden im unteren Bereich des Temperaturprogramms im Gegensatz zu Dexil Methan, Äthylen und Äthan zurückgehalten. Nach Erprobung einer Reihe anderer Säulenfüllmaterialien können wir zusammenfassend sagen, daß die Probennahme mit dem Thermogradientrohr recht spezifisch erfolgen kann, wobei das Ausmaß der Spezifität von der Art des verwendeten Sorptionsmaterials abhängt. Hieraus ergibt sich, daß in keinem Fall alle in der Luft befindlichen Komponenten in einem Analysengang zu erfassen sind. Dies ist im Hinblick auf eine selektivere Detektion der Komponenten wegen ihrer außerordentlichen Vielzahl durchaus wünschenswert. Für den Analytiker bedeutet diese Tatsache jedoch, daß je nach der erwünschten Information das Sorptionsmaterial dem jeweiligen Analysenproblem in optimaler Weise angepaßt

TABELLE 1

Massenspektrometrisch identifizierte Komponenten

Methan
Methanol
Dichlormethan
Methylchlorid
Freon 22 (CF_2ClH)
Freon 12 (CF_2Cl_2)
Äthan
Äthanol
Äthylen
Aceton
Trichloräthylen
Tetrachloräthylen
Fluor-1, 1-Dichloräthan
Propan
Butan
Buten
Butin
Isobutanol
Diäthyläther
Pentan
Penten
Pentadien
Hexan
Benzol
Trichlorbenzol
Heptan
Toluol
Oktan
p-Xylol
m-Xylol
o-Xylol
Trimethylbenzole
Methyläthylbenzol
Chlorbenzol
Dichlorbenzol

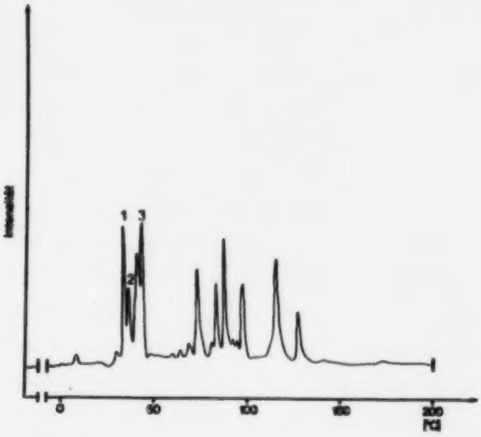

Abb. 3. Verwendung von Porapak Q als Sorptionsmittel im Thermogradientrohr. 1 Methan; 2 Äthylen; 3 Äthan.

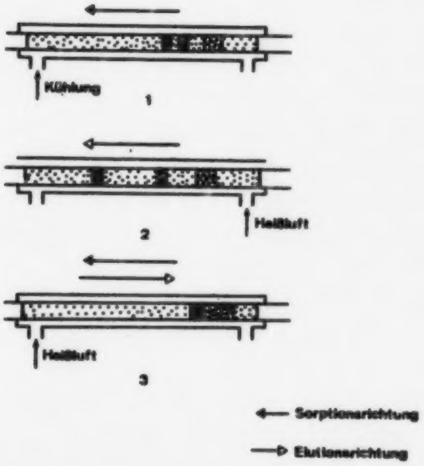

Abb. 4. Schematische Darstellung der chromatographischen Vorgänge auf dem Thermogradientrohr bei der Probenanreicherung (1) sowie bei der Probenelution ohne Umkehr der Betriebsrichtung (2) und mit Umkehr der Betriebsrichtung (3) im Gradient.

werden muß.

Hatten uns unsere Untersuchungen gezeigt, daß die Füllung des Thermogradientrohres den für die qualitative Analyse wichtigsten Faktor dieser Untersuchungsmethode darstellt, so schien es uns zumindest von theoretischem Interesse, die Vorgänge im Thermogradientrohr während der Probennahme und besonders während der Probenaufgabe zu untersuchen. Wie Abb. 4 verdeutlicht, besteht das Thermogradientrohr aus zwei konzentrischen Röhren, wobei das innere Rohr einer klassischen gepackten gaschromatographischen Trennsäule entspricht. Während der Probenahme wird nun der äußere Mantel im Gegenstrom mit dem Dampf von flüssigem Stickstoff gekühlt, bei der anschließenden Probenaufgabe wird dieser Mantel - ebenfalls im Gradienten - mit Heißluft auf 220 °C erwärmt. Dabei werden die retinierten Substanzen mit einem Trägergasstrom auf die gekühlte gaschromatographische Säule eluiert. Erfolgt die Elution in der Ansaugrichtung (Abb. 4 Mitte), so wird eine bereits während der Probennahme erreichte gaschromatographische Vortrennung der Komponenten verstärkt. Eluiert man jedoch entgegen der Ansaugrichtung (Abb. 3 unter) so wird diese Vortrennung wieder aufgehoben. Derartige Vorgänge auf der Trennsäule konnten wir dadurch dokumentieren, daß wir das Thermogradientrohr während der Elution direkt mit den jeweiligen Detektoren koppelten. Über Einzelheiten dieser Versuche haben wir an anderer Stelle berichtet [4]. Zur Verdeutlichung der Vorgänge auf dem Thermogradientrohr sei hier lediglich das Ergebnis einer Elution in Sorptionsrichtung (Abb. 5) und entgegen der Sorptionsrichtung (Abb. 6) demonstriert. Man erkennt deutlich, daß die im ersteren Fall eingetretene Vortrennung bei Umkehr der Elutionsrichtung wieder aufgehoben wird. Dieses Faktum ist insofern von Bedeutung, als die Vortrennung der Komponennten auf der Thermogradientsäule prinzipiell eine noch spezifischere Aufgabe ermöglichen sollte, indem z. B. eine

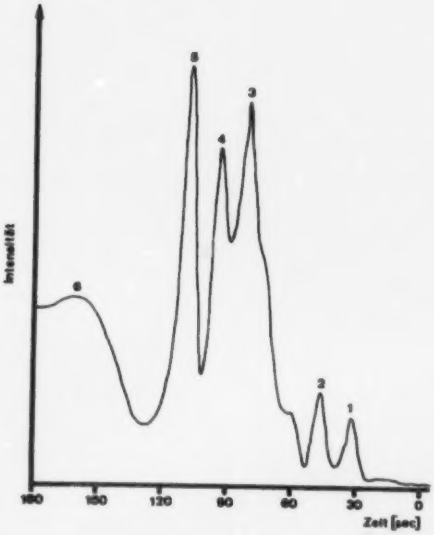

Abb. 5. Elutionschromatogramm durch direkte Kopplung des Thermogradientrohres an den Detektor (FID). Die Elution erfolgt ohne Umkehr der Betriebsrichtung. Stationäre Phase: Dexsil GC 300. 1 Pentadien; 2 Benzol; 3 Toluol, Tetrachloräthylen; 4 Xylole; 5 Trimethylbenzole; 6 Wasser.

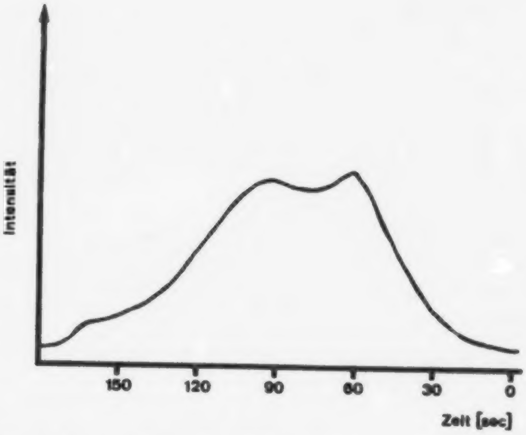

Abb. 6. Elutionschromatogramm durch direkte Kopplung des Thermogradientrohres an den Detektor (FID). Die Elution erfolgt mit Umkehr der Betriebsrichtung. Stationäre Phase: Dexsil 300 GC.

vorgetrennte Substanzgruppe durch Umleitung des Trägergasstromes allein auf die gaschromatographische Trennsäule aufgebracht werden könnte. Auf diese Weise ließe sich z. B. das im EID-Chromatogramm störende Wasser abtrennen. Inwieweit sich die auf dem Thermogradientrohr festgestellte Vortrennung auf das endgültige Trennergebnis auswirkt, kann an dieser Stelle noch nicht diskutiert werden. Diesbezügliche Untersuchungen werden von uns momentan durchgeführt.

Zusammenfassend und ausblickend ist damit festzustellen: Bei der von uns verwendeten Technik erfolgt die Probennahme mehr oder minder spezifisch. Je größer die Spezifität der Probennahme und -aufgabe, desto geringer wird bei gleichem apparativem Aufwand jedoch der Informationsumfang. Gleichzeitig wird aber die gewünschte Selektivität des Nachweissystems erhöht. In Zukunft wird allerdings die Erhöhung der Trennleistung durch Verwendung von Trennkapillaren bzw. die Anwendung von selektiveren Detektoren, wie der Massenspektroskopie und besonders der Massenfragmentographie, eine unspezifischere Probennahme und damit eine Erhöhung des Informationsumfanges zulassen. Dadurch wird einmal die Möglichkeit gegeben, eine Bestandsaufnahme der oft in Ultraspurenkonzentrationen vorliegenden Umweltschadstoffe durchzuführen. Zum anderen erlaubt der periodische Einsatz der Methode wegen der ihr eigenen niedrigen Nachweisgrenzen die frühzeitige Erkennung neu in die Atmosphäre gelangender Noxen. Sie bietet einen echten Ansatzpunkt für ökopräventive Maßnahmen,indem beim ersten Auftreten neuer Schadstoffe Gegenmaßnahmen zu einem Zeitpunkt getroffen werden können, zu dem mit einem noch verhältnismäßig geringen Aufwand gravierendere Umweltgefahren durch die spezifische Noxe verhindert werden können.

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DISKUSSION

HARKE (Bundesrepublik Deutschland)

Ich möchte Sie fragen, ob die vorgestellte Methode geeignet ist

a) quantitative Bestimmungen durchzuführen
b) Aerosole aus leichtflüchtigen Substanzen in Raumluft zu bestimmen.

ANGERER (Bundesrepublik Deutschland)

a) Zu Ihrer ersten Frage möchte ich bemerken, dass es durchaus möglich ist, mit dieser Methode quantitative Bestimmungen durchzuführen. Dies ist ein Problem der Eichung. Es gibt dafür prinzipiell folgende Möglichkeiten:

   - Bekannte Konzentrationen, möglicherweise Gemische interessierender Stoffe werden in gleicher Weise wie die zu bestimmenden Luftproben aufgearbeitet und analysiert. Dadurch lässt sich eine Eichkurve für diese Stoffe erstellen;

   - Die zu analysierende Luftprobe wird vor Ihrer Anreicherung aus dem TG-Rohr in einem definierten Volumen gesammelt. Dazu gibt man eine bestimmte Menge eines gleichsam als innerer Standart dienenden anderen Stoffes. Aufgrund der spezifischen Empfindlichkeiten der verwendeten Detektoren gegenüber diesen Stoffen lassen sich nun die Konzentrationen der einzelnen Stoffe berechnen;

   - Die von R. Kaiser vorgeschlagene Möglichkeit einer "absoluten Eichung", die ebenfalls auf den spezifischen Detektorempfindlichkeiten beruht, lässt ebenfalls eine Konzentrationsbestimmung der einzelnen Stoffe zu.

b) Zu Ihrer zweiten Frage möchte ich sagen, dass wir noch keine Erfahrung mit Aerosolen sammeln konnten.

PERRY (United Kingdom)

Wenn das von Ihnen beschriebene Verfahren dazu benutzt wird, einen spezifischen organischen Stoff in der Atmosphäre zu messen,wie wollen Sie das System eichen?

ANGERER (Bundesrepublik Deutschland)

Zu Ihrer Frage ist festzustellen, dass dieses Verfahren dazu dienen soll, nicht nur eine sondern gleichzeitig eine Vielzahl von organischen Spurenkomponenten spezifisch in der Atmosphäre zu messen. Was das Problem der Eichung betrifft, darf ich Sie auf meine diesbezüglichen Äusserungen Herrn Dr. Harke gegenüber verweisen.

PFANNHAUSER (Austria)

Wie haben Sie versucht, die mögliche Störung durch Wasser auszuschalten?

ANGERER (Bundesrepublik Deutschland)

Bei der Verwendung eines Flammenionisationsdetektors stellt das aus dem TG-Rohr kondensierte Wasser kein analytisches Problem dar, da der FID bekanntlich Wasser nicht anzeigt. Dies zeigt im übrigen auch Abb. I.

Allerdings muss bei der Verwendung eines Wasserspektrometers eine Trockenstrecke vor das TG-Rohr geschaltet werden, da anderenfalls das für die qualitative Analyse notwendige EID-Leitchromatogramm empfindlich gestört werden würde.

BRAMAM (U.S.A.)

Flüssiger Stickstoff kann die leichten Kohlenwasserstoffe quantitativ ausfrieren. Die Methode bietet ausgezeichnete Möglichkeiten.

ANGERER (Bundesrepublik Deutschland)

Zunächst darf ich mich für Ihre freundliche Bemerkung bedanken, da auch wir von den Möglichkeiten dieser Methode überzeugt sind. Ich darf Sie jedoch darauf hinweisen, dass nicht flüssiger Stickstoff, sondern dessen Dampf bei dieser Analysenmethode verwendet wird. Ausserdem handelt es sich bei der Anreicherung der Substanzen aus dem TG-Rohr um einen gaschromatographischen Vorgang, nicht primär um ein Ausfrieren der Komponenten.

Ich darf jedoch an dieser Stelle sagen, dass wir augenblicklich an einer Methode arbeiten, bei der die Komponenten tatsächlich mit flüssigem Stickstoff ausgefroren werden. Diese Methode wird eine Ergänzung der geschilderten Methode darstellen.

IMPROVED METHODS OF SAMPLING AND ANALYSIS OF AIRBORNE HAZARDOUS PARTICULATE POLLUTANTS

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ABSTRACT

Studies based on classical air filtration sampling have neglected to consider losses due to the volatility of the compounds sampled. A class of hazardous air pollutants among them PAH, arsenic oxides, selenium oxide show vapor pressures which raise serious doubts about the validity of air quality data for this class of compounds.

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The collection, identification and measurement of airborne particulate matter continues to be one of the primary goals of environmental assessment surveys. A great variety of inorganic and organic pollutants, some posing a hazard to human health, are collected, ordinarily, by air filtration and analyzed by a variety of techniques. Most attention has been focussed upon those compounds whose published biological activity has suggested carcinogenicity or toxicity at ambient air levels. Notable among these "hazardous" pollutants are the PAH and compounds of arsenic, selenium and mercury.

Classical methods for the determination of compounds of arsenic, selenium and mercury are being upgraded with respect to sensitivity and accuracy by procedures which include concentration and chelation steps and highly specific ultraviolet photometry. For the separation and determination of the various PAH, a number of analytical schemes have been published. Characteristic of these analytical procedures are combinations of extraction, chromatography, spectroscopy using ultraviolet absorption or optical fluorescence.[1,2] Most recently, the technique which uses gas chromatography, mass spectrometry and automatic data processing as the total instrument, has been successfully applied to PAH analysis.[3,4]

While the analytical techniques for pollutant assessment have continually undergone evaluation and improvement, few changes or investigations have been made with respect to the methodology of the collection of the pollutants from the ambient air. Traditionally, airborne particulates have been sampled by drawing a known volume of contaminated air through filters made of glass fibre, cellulose or organic membranes. The particulate matter, entrained on the filter, has then been assayed. The fact that simple air filtration sampling has been so universally applied as a standard procedure for such a long period of time, without any attempts at re-evaluation, has serious implications. It must be realized that a number of particulate pollutants, having high vapor pressures, will either pass through the filter medium without being trapped or they may be evaporated from the collected particulates with the continuing passage of the air stream.

A few studies of the volatility of some PAH have been made in the past and some vapor pressure data have been published. However, these studies were cursory in nature and the accuracy of the results is suspect. Recently the "equilibrium vapor pressures" of some PAH were determined.[5,6] The compounds investigated were benzo(a)-anthracene (BaA), benzo(a)pyrene (BaP), benzo(e)pyrene (BeP), benzo(k)fluoranthene (BkF), benzo(g,h,i)perylene (BghiP) and coronene. These PAH were chosen, by the International Association for Research on Cancer, as the PAH which should be analyzed in any program of monitoring the PAH content of air. The compounds in question exhibit vapor pressures in the range 10^{-8} to 10^{-4} atmospheres over a range of 70 to 150°C.[5] The equivalent vapor pressures at the ambient temperatures can be estimated by the least squares fitted equation,

$$\frac{\log_{10}P}{(\text{atm})} = -\frac{A}{T} + B$$

The concentrations of PAH, as found in air, are usually reported in micrograms per 1000 cubic metres. The ranges of published concentrations of PAH in ambient air at 25°C[1] are given below, with the corresponding equilibrium vapor concentration (EVC) calculated from the equilibrium vapor pressure (EVP):

compound	µg/1000 m^3	evc
pyrene	1.3-35	74,000
BaA	0.1-22	1,050
BaP	0.2-39	85
BeP	1.0-26	85
BkF	1.0-20	16
BghiP	2 -46	1.6
coronene	0 -20	0.1

It is clear that, except for coronene and possibly BghiP, vapor losses on sampling may be appreciable. There are two effects which can reduce losses below those represented by the EVCs of the pure substances. Firstly, the EVCs may not be reached due to a slow rate of vaporization; secondly, the pollutant may be adsorbed on an active particulate substrate and its EVC, in this state, may be significantly less than for the pure state. The kinetic effect of slow vaporization is considered to be small and has its effect mainly on the rate of loss of material already collected on the filters. On the other hand, even when the EVCs are reduced by adsorption effects, the EVCs of the pure substance give a relative measure of the volatility and corresponding inefficiency of collection. However, since adsorption is not immediately effective[6], vapor concentrations of PAH and compounds of arsenic, selenium and mercury encountered during emission measurements are probably of the order of the EVCs regardless of the presence of soot or other particulates.

Failure to collect a concentration equal to the vapor concentration and subsequent sublimation from the filter are sources of error in high volume sampling. A measurement, based on particulate sampling, should be considered uncertain by an amount equal to the EVC unless réduction of the EVC by the effects of adsorption can be established.

A series of experiments have been designed in this laboratory to assess the influence of temperature, air flow rate, vapor pressure and adsorption effects upon the collection efficiency of the air filtration sampling technique for particulate contaminants which have been found in air. The first system investigated was arsenic oxide. In this experiment, the filtration sampler was connected to a Greenburg-Smith impinger, containing sodium hydroxide solution, in order to collect gaseous As_4O_6 which escaped from the filter medium. Details of the apparatus procedures and results are given in a recent paper.[7] The equilibrium vapor pressure (EVP) of As_4O_6 was calculated from

$$\frac{\log_{10} P}{\text{atm}} = - \frac{6067}{T} + 9,905$$

The date quoted or calculated from a generally accepted reference handbook[8] can generate serious errors[7] due in part to the fact that arsenic oxide does not exist in the gaseous state as As_2O_3 but as As_4O_6.

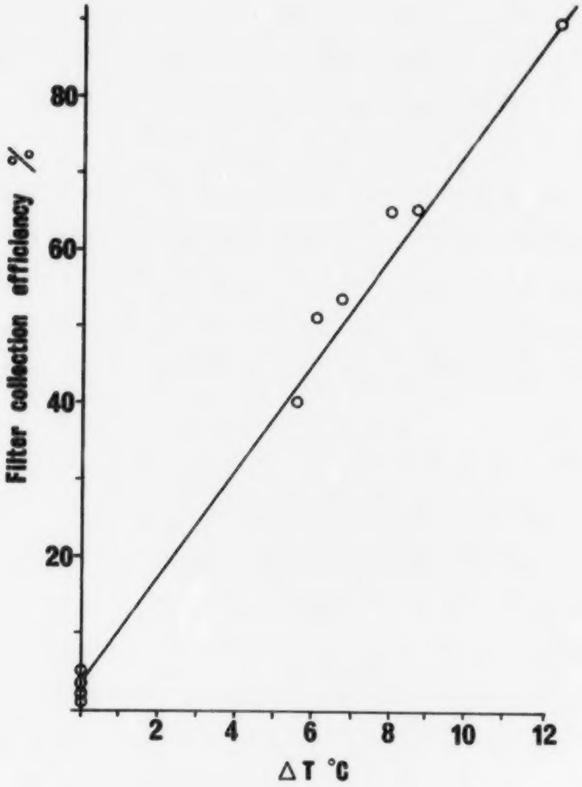

Fig. 1. Calculated filter collection efficiency from EVP

Figure 1 illustrates the filter collection efficiency as calculated from the EVP and represents the minimum theoretical efficiency for the temperature differential, ΔT, between the temperature of a pure sample of As_2O_3 and the filter. The experimental results in Figure 2, obtained by dividing arsenic trioxide on the filter by the sum of arsenic trioxide on filter plus arsenic trioxide in the absorbing solution, indicate that for the same ΔT, the EVC for As_2O_3 is lower than that calculated from theory. Due to variations in the uncontrolled ambient temperatures over the long experimental period, the data points deviate from the normal straight

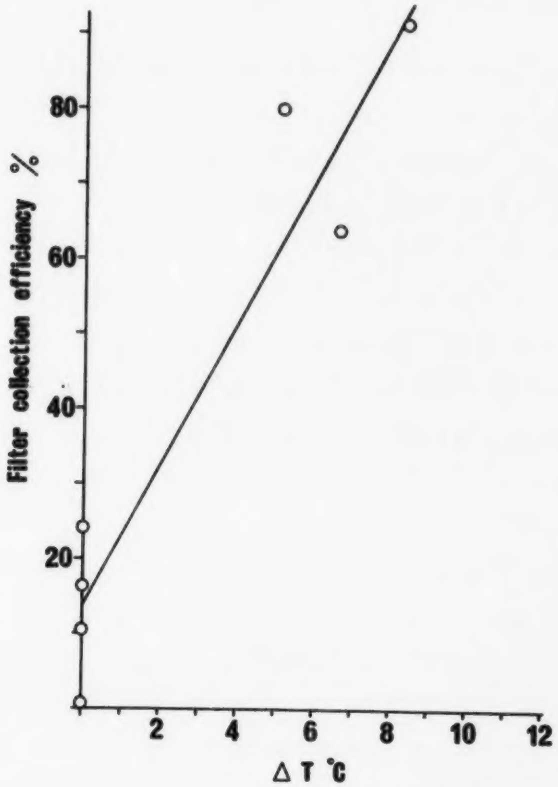

Fig. 2. Experimental filter collection efficiency from EVP for As_2O_3.

line relationship. However, in spite of these deviations, the temperature dependent relationship of collection efficiency holds. Therefore, the air filtration sampling technique for particulate arsenic compounds is unsatisfactory when the temperature differential between filter and ambient air is small. The same is true for other airborne particulates which have an appreciable EVC.

Work is under way to design a very precisely temperature controlled apparatus, to assess the adsorption of pollutants or particulates and to investigate the evaporation of such pollutants while trapped on filter media. It is hoped that such investigations may lead to quantitative improvements in the sampling of important pollutants, whose fundamental chemical and physical properties ensure anomalies in sampling.

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DISCUSSION

RONDIA (Belgium)

The work of Commins and of our laboratory have shown already sometime ago the volatility of polycylic hydrocarbons with relatively low boiling point. This work has recently been resumed and shows that the organic material present in air escapes normal sampling using high volume samplers such as the Staplex. A large number of substances with a boiling point below 350°C are retained on the filter as a function of the air temperature and the length of sampling.

This could invalidate, for example, the results from the national network of the U.S.A. as regards soluble benzene. Similarly, in our countries the difference of BaP concentration in air between winter and summer has been unanimously attributed to domestic heating. Present experience shows that other factors, such as sampling method, are involved, and that industrial sources (particularly in Liège where this study was carried out) also undoubtedly play an important rôle.

LAO (Canada)

I agree with you.

BUSH (U.S.A.)

Did you have any difficulty separating BaP from BeP on your gas-chromatographic columns?

LAO (Canada)

There is no difficult if only BeP is separated from BaP. However, if a sample has more than 70 or 80 compounds, BeP will not separate from BaP under normal gas-chromatographic conditions (e.g. use only one column). In our experiment when BaP and BeP are in a same fraction and BaP is determining quantitativly by fluorescence spectroscopy the amount of BeP is then obtained by subtraction.

KUMMER (Belgium)

Would not the addition of an activated carbon filter enable the polycyclic aromatic hydrocarbons to be collected more effectively?

LAO (Canada)

We have not tested this method. Perhaps it will be difficult to recover all PAH entrained on an activated carbon filter.

SHERWOOD (U.K.)

The problem of evaporation of particles from air sample filter papers can also occur when sampling mineral oil mists. Although vapour can be collected by a silica gel trap placed behind the filter, this does not distinguish between ambient vapour concentration and vapour released from particles on the filter.

LAO (Canada)

Yes, if the total vapour concentration does not reach the "equivalent vapour concentration" at the ambient temperature, particles collected on the filter will evaporate.

SURFACE AREA AND ADSORPTION PROPERTIES OF DUST PARTICLES

W. KARCHER, P. GLAUDE, R. DEPAUS

Euratom, CCR Petten, the Netherlands

ABSTRACT

The surface area and adsorption capacity for benzene and naphtalene has been determined for two natural dust specimens which were obtained by filtration or impaction in an urban (Milan) and rural (Ispra/Varese) area respectively. To distinguish between the adsorption properties of the bulk samples and the respirable size fraction, the same measurements have been repeated for the size fraction with a particle diameter $< 5\ \mu m$.

The results indicate only marginally higher specific surface areas for the small size fraction than for the bulk specimens. Also, the amount of hydrocarbons which can be adsorbed at normal pollution levels ($< 1 mg/m^3$) *is so low* ($< 1\ \mu g/g$) *that pollutant removal by a pure adsorption process on dust or aerosol particles, as it has been discussed repeatedly in the literature, seems rather unlikely.*

1. Introduction

Repeatedly it has been suggested in the literature as a result of adsorption measurements at very high partial pressures of pollutants (> 1 g/m^3), that certain atmospheric pollutants may be removed from the atmosphere by an adsorption process on airborne particulate matter (1,2). Though a recent theoretical study has shown that rather high surface areas would be required for an appreciable rate of removal by an adsorption process (3), no definite conclusions can be drawn from the available literature data, since no adsorption measurements had been performed at concentrations corresponding with natural pollution levels. To fill this gap, some adsorption measurements have been carried out with benzene and naphtalene in the concentration range of 0.3 - 50 mg/m^3 (average atmospheric concentrations 0.05 - 1 mg/m^3) on dust particles which had been precipitated from the atmosphere by impaction or filtration. To this effect, the break-through curves of benzene or naphtalene in a stream of carrier gas have been measured at room temperature on two dust specimens which had been obtained in an urban (Milan) and rural (Ispra) area respectively. The surface area for the total dust samples and for the respirable size fraction (< 5 m) has been measured with the conventional BET-method (4).

2. Experiments

For the adsorption and surface area measurements, two dust specimens have been selected, which had been obtained by filtration or impaction in an urban area (Milan) and rural area (Ispra) respectively. The results of a qualitative chemical analysis of the two specimens are presented in table I. It is evident from these figures, that the urban dust sample contains much more carbon, but considerably less inorganic material (SiO_2, Al_2O_3, CaO) than the specimen which was obtained from a rural site.

Table I

Chemical Analysis of Dust Specimens

Constituent	Urban	Rural Sample
	(weight percent)	
C	> 40	16,2
H	1,7	2,25
N	1,9	1,33
SiO_2	12,9	32
Al_2O_3	3,8	5,7
Fe_2O_3	5,6	8,6
CaO	7	14
MgO	0,8	
Zn	1,3	1,25
TiO_2	0,4	0,7
PbO_2	0,9	
NiO	0,3	0,4

(The trace metals are shown arbitrarily as oxides)

The adsorption experiments have been performed in a fixed bed arrangement under flow conditions with a dust specimen of 0,2 - 0,3 g at room temperature (after degassing at room temperature), using calibrated gas mixtures air/benzene or helium/benzene at a flow rate of 2.65 ml/min. The hydrocarbon concentration in the exit stream has been measured by gas-chromatography with a flame ionisation detector. From the resulting break-through curves the break-through time has been derived graphically and the corresponding dynamic adsorption capacity calculated accordingly.

Table II

Surface Area of Rural and Urban Dust Specimens

Sample	degassed at			
	25°C		300°C	
	surface area (m^2/g)	micro porosity (cm^3/g)	(m^2/g)	(cm^3/g)
Rural (orig.)	2,2		10,8	
(<5 μm)	2,6		6,3	
Urban (orig.)	2,5-3,0	$1,9.10^{-3}$	11-12	$9,4.10^{-3}$
(1-5 μm)	3,9		11,9	
(>5 μm)	3,1		8,8	
(orig. after extraction with C_6H_6)	5,3	$4,6.10^{-3}$	11,8	1.10^{-2}

The BET-surface area has been determined volumetrically by argon adsorption at -196°C after the specimen had been degassed at room temperature or 300°C under vacuum. In some instances, the micropore size distribution curves have been calculated from the complete argon adsorption-desorption isotherms by means of the BJH-method (5) The micropore volume measured in this way is indicated in table II.

3. Results

The results of the surface area measurements are given in table II. It can be seen that the surface area for both dust specimens varies between 2 and 4 m^2/g, with the respirable size fractions with a particle diameter < 5 µm showing only slightly higher surface areas than the original dust samples. After degassing at 300°C, 3-4 times higher surface areas are obtained, indicating a release of some adsorbed or constituent species under degassing at 300°C.

As it is to be expected from these relatively low specific surface areas, the evaluation of the break-through curves indicates a very low dynamic adsorption capacity of the dust specimens of benzene concentrations which are comparable with atmospheric conditions. For instance, at a benzene partial pressure of 1 mg/m^3 and under flow conditions (13,5 cm/min) an adsorption capacity of approximately 10^{-2} and 0.3 µg/g has been derived from the break-through curves for the urban dust specimens for C_x/C_o = 0.01 and

0.8 respectively (C_x and C_o denote the benzene concentration at the in- and outlet of the dust bed). Even at a dust level of 1 mg/m^3 no measurable concentration effect due to benzene adsorption on dust particles would be evident under these circumstances, since per unit volume of air less than 10^{-4}% of the original partial pressure of benzene would be adsorbed on airborne particles.

The dynamic adsorption capacity of the urban dust specimen for benzene vapour has been plotted in fig. 1 for C_x/C_o ratios between 0.01 and 0.8 as a function of benzene concentration in air. The adsorption isotherms

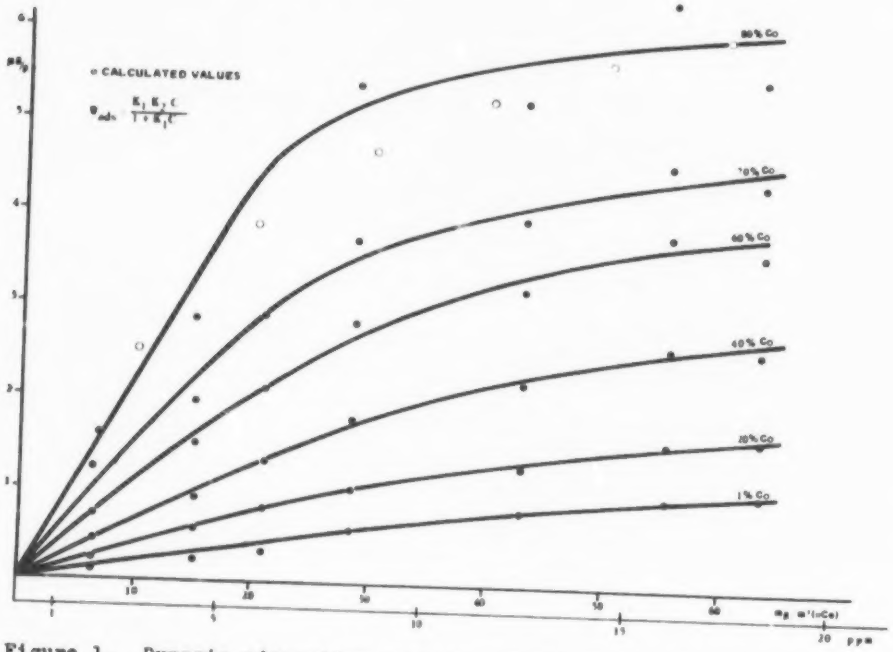

Figure 1. Dynamic adsorption capacity of Milan dust as a function of Benzene partial pressure.

obtained in this way resemble closely a Langmuir-type adsorption isotherm so that the amount of benzene adsorbed (W_a) for any given benzene partial pressure (C) may be calculated with good accuracy by means of the equation

$$W_a = \frac{K_1 \ K_2 \ C}{1 + K_1 C} \qquad (1)$$

The break-through curves of naphtalene obtained on the urban dust specimen in the concentration range 0.5 - 50 mg $C_{10}H_8/m^3$ are comparable to those of benzene. However, at comparable partial pressures, naphtalene is retained about 10 to 100 times more effectively than benzene (see fig. 2). But even for naphtalene, less than 0.1‰ of the concentration in the vapour phase would be in the adsorbed state at a dust and hvdrocarbon level of 1 mg/m^3.

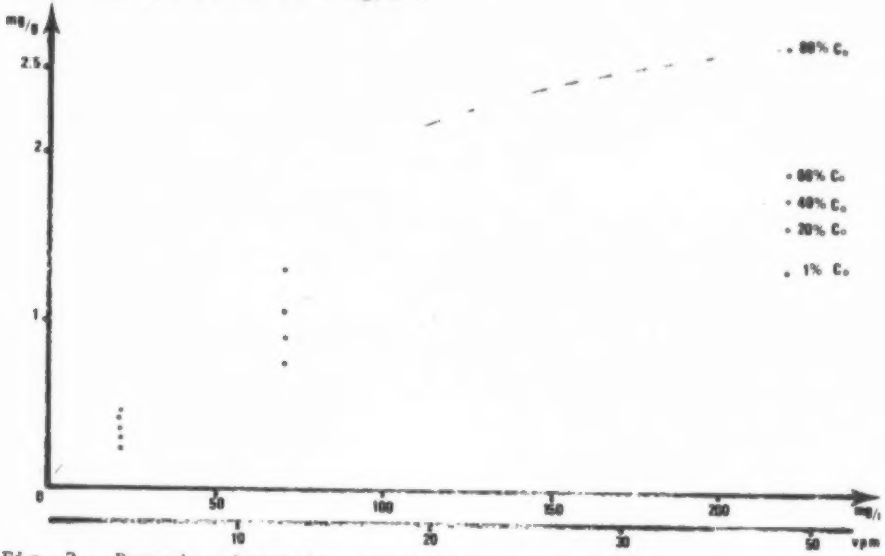

Fig. 2. Dynamic adsorption capacity of Milan dust in presence of naphthalene.

From these results it must be concluded that at normal atmospheric dust levels removal of gaseous pollutants due to adsorption alone on airborne particles seems highly unlikely. This estimate does not take into account adsorption phenomena by soil and plant surfaces, where much higher surface areas are available. Also, chemical reactions on catalytically active dust particles may very well contribute significantly to removal or transfer processes of specific gaseous pollutants in air.

Acknowledgments

The dust samples and analytical data have been obtained by courtesy of Messrs. Geiss, Versino and Zamorani from Euratom CCR Ispra, Chemistry Division.

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DISCUSSION

HARRISON (U.K.)

I am referring to your chemical analysis data in Table I. Various metals are listed as their oxides. I would like to know whether any evidence was obtained to the effect that these metals were in fact present in air as their oxides. The presence of Pb in urban particulates as PbO_2 (0.9% of total weight) would be particularly surprising.

KARCHER (C.C.R. - Petten)

The dust specimens have been provided and analysed by Euratom, CCR Ispra. As far as I know the inorganic components have been analysed by means of neutron activation analysis, polarography and X-ray diffraction. The metals have been presented arbitarily as oxides and have not been analysed with regard to chemical composition since in view of the large number and low concentrations of trace metals present in the samples the task of identifying the chemical nature of the numerous constituents would have been very difficult indeed.

AN IMPROVED TECHNIQUE FOR MONITORING PARTICULATES IN THE ATMOSPHERE TO CHECK AIR QUALITY STANDARDS

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Central Environmental Management Service Rijnmond, Schiedam,
The Netherlands

ABSTRACT

Standards for allowable concentrations of toxic substances in ambient air often appear to be incompatible with available measuring methods and apparatus. In the US there is a tendency to combine air quality standards with an analytical method. On the other hand the Dutch proposed standard for SO_2 *is coupled with the particulate-concentration, which should be expressed in units of standard smoke according to the OECD specification of 1964. When an air quality standard does not indicate a measuring method, the method should be adjusted analytically or technically to that standard.*

The council of Rotterdam declared an air quality standard for particulates in 1970, when south of Hook of Holland an iron-ore terminal started to operate. This standard was clearly inspired by the US standard proposal and the American method of using high volume samplers. In the given regulations was laid down, that by exceeding the standard, activities of the iron-ore terminal should be stopped. This implied continuous monitoring. Because there was no commercially available apparatus that fulfilled the needed requirements, an adequate instrument was developed, to meet the following requirements:

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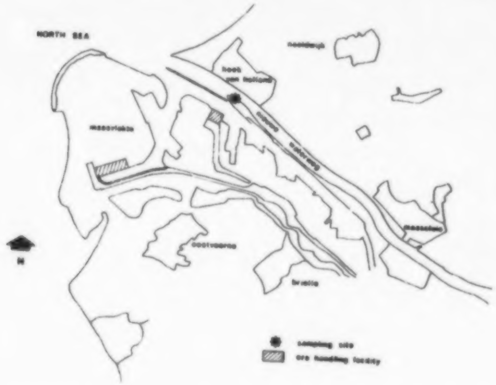
1. *The apparatus must be operating continuously.*
2. *Contamination of the filters by the sampler-motor must be avoided.*
3. *Periods between servicing must be as long as possible.*
4. *The instrument should have a constant flow device.*
5. *Inserting new filters in the filter holder must be done in the laboratory to prevent unnecessary damages of the filter.*
6. *Linear air velocity and amount of sucked air must be comparable with that of commercial apparatus.*

A description of the instrument is given and some monitoring results are discussed.

1. Introduction

After the second world war the port of Rotterdam has expanded enormously. Because of its favourable geographical situation at the mouth of the river Rhine a large number of refineries and petrochemical industries has settled on sites west of the city of Rotterdam. The reclamation of about 24 square kilometers of land from the sea in front of the original coastal line offered new possibilities to industries, dependant on deep water for the supply of raw materials. This area, called Maasvlakte, can be reached by ships up to 240.000 tons (figure 1). The possible establishment of steel works in 1970, combined with coal and ore handling facilities, made the problem of contamination by particulates acute. The fear for suspended particulate matter was dictated by the known synergistic effects with sulphur dioxide (Amdur [1]) and the catalytic action of iron and other metals upon the oxidation of sulphur dioxide (Bracewell [2]). Because of this reason together with infrastructural problems, the original plan for the steelworks has been withdrawn. However, newcoming coal- and ore handling companies were faced with an air quality standard for particulate matter, that had not to be exceeded in neighbouring living areas. This standard relates to measurements with a sampling time of 24 hours over a period of one year and contained the following limits [3, 4]:

50 percentile (median value)	80 $\mu g/m^3$
75 percentile	120 $\mu g/m^3$
98 percentile	240 $\mu g/m^3$.



Location of samplingsite and ore handling facilities.

The standard has been inspired by the use of sampling with commercially available high volume samplers, but neglected the limited reliability and serviceability of these samplers. In the first year the monitoring has been done continuously, because it was not clear whether at random sampling provided a fair estimate of the 98 percentile. Selected data of the first year of monitoring show that the estimated 98 percentile value was inaccurate. For this reason monitoring had to be continued on the same continuous base and the high volume samplers had to be adapted to this purpose.

2. Design of an improved High Volume Sampler

The main objections against the available high volume samplers are:

1. The flow rate measurement by means of a rotameter device is not accurate. The rotameter measures only a small proportion of the total flow through the sampler.
2. The total amount of sampled air after a sampling period of 24 hours is determined by a flow rate measurement at the beginning and the end of the sampling period. Usually a linear decrease in flow rate is assumed. However, the decrease in flow rate is related to the filter loading and - at least in the Rijnmond area - a relative strong decrease in flow rate can be expected between 8 and 10 a.m.
3. In the high volume samplers known to us, collector motors up to 20.000 r.p.m. are used. It appeared, that they are not suitable for continuous use because of their limited life time. Fast rotation wears down the motor quickly. Collector wear frees copper, that is monitored eventually. The abrasion of the carbon-brushes originates carbon, that possibly influences the filter loading. The life of the carbon-brushes varied in extreme cases between one day up to one month.
4. Due to the fact that the sampling site and laboratory were relatively at a distance, the filters were changed by people working in the vicinity of the site. Their initial enthusiasm slackened after some time.
5. Filter changing and transportation of the filters to the laboratory often caused damage of filters.

The disappointing experiences with the available high volume samplers and the need for automation were the main reasons for

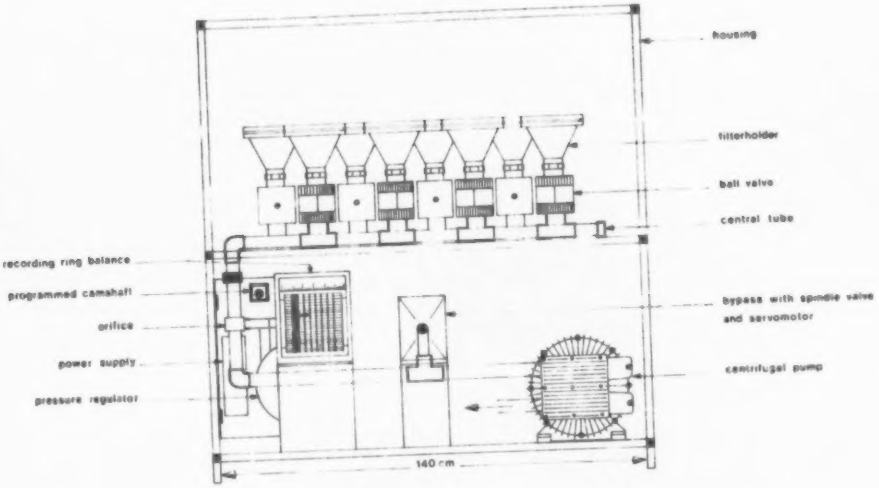


Fig. 2. Front-view of the high volume sampler

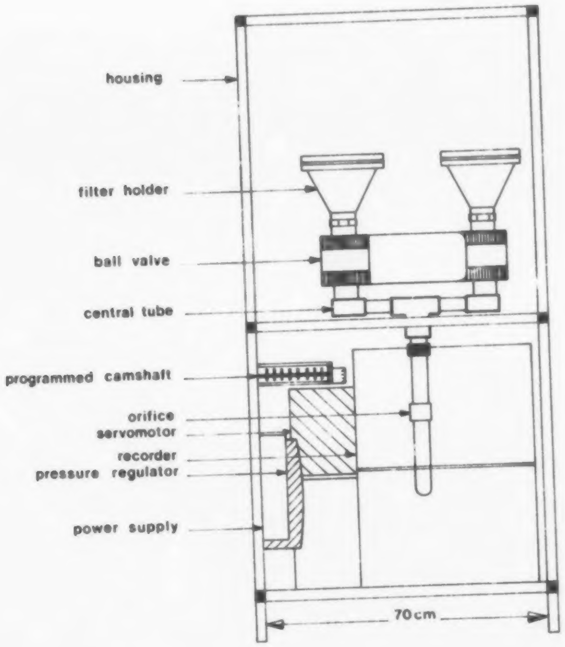


Fig. 3. Side-view of the high volume sampler

developing a new sampler with the following requirements:

1. The apparatus must be operating continuously.
2. Contamination of the filters by the sampler-motor must be avoided.
3. Periods between servicing must be as long as possible.
4. The instrument should have a constant flow device to keep the mass by unit of time of monitored air constant.
5. Inserting new filters in the filterholder must be done in the laboratory, just to prevent unnecessary damages of the filter.
6. The specifications of the developed apparatus should be the same as for other high volume samplers, especially with respect to the lineair velocity of sampled air (Jutze [5], Sholtes [6]).
7. Preference should be given to commercially available parts.

Regarding the first three requirements, the choice of the pump is essential. The system should meet the need of unattended running for a year, sucking a sufficient and constant air flow and hardly any emission of carbon particles, copper or other metals from the pump should take place. Motors of the current collector type are less suitable. A single or three-phase AC motor with a two stage compressor can meet the requirements.

A typical example is a centrifugal pump of 1,5 hp, 2800 r.p.m. displacing 3 m^3/min when running unloaded and operating down to 0,8 ata. A disadvantage of this pump is, that the volume of the transported air cannot be regulated by voltage control: variations of more than 10 volts result in a sharp decrease of the volume of passed air. Therefore the air flow is controlled by using a bypass regulator (figure 2, 3). A P.V.C. spindle valve, with 20 turns from open to close, inner diameter 40 mm, is used as a bypass, because of the availability and the easy fitting qualities with the existing tubing. The valve is regulated by a servomotor, making one rev/min. The bypass only works effectively in the last 6 turns of the spindle-valve, so it takes less than 6 minutes before a maximum disregulation has been adjusted completely. Two micro switches are safe-guarding the valve by deactivating the servomotor at extreme settings of the valve.

Measuring air flow rate through the filter seemed to be optimal by means of an orifice. Variations of the differential pressure over this orifice should be translated into an electrical signal. One of the possibilities consists of using a flowmeter parallel to the orifice and catching the movements of the floater by two lightbeams and fotocells. A disadvantage of this construction is that a variation in a small part of the total air stream is regulating the bypass system. Furtheron fast flow changes disarrange the system. However, a static pressure regulator, used in a differential pressure sensing mode, offered a useful alternative. It causes an electrical signal, becoming larger the more the differential pressure is drifted from a preset value. This signal controles the servomotor. Deviations of less than 5 % from the equilibrium are corrected, but the effect of the decreasing absolute pressure is neglected, when the resistance of the filter grows with increasing loading. By neglecting these effects an error of maximum 10% is introduced. In the actual monitoring situations, however, the error is less than 5 %.

The mentioned regulation of the flow is effective under chosen conditions up to 300 $\mu g/m^3$ particulate matter as a daily mean value. This means a filter loading of 150 mg. Underestimation of the particulate concentration occurs, when more than 300 $\mu g/m^3$ as a daily mean value is present. With this pressure regulation system the second requirement has been met. Moreover the differential pressure over the orifice is recorded.

Inserting new filters should be kept to a minimum; that means that the sampling site is visited once a week.

Figure 2 shows that 8 filterholders are connected via 8 ball-valves to a central tube. The ball-valves are opened and closed by a programmed camshaft, controlling micro switches. The switching procedure takes about 30 seconds. To prevent overload of the pump, one valve is gradually closed and at the same time the next valve is slowly opened.

The construction of the filter holder is shown in figure 4. To obtain a favourable effect on the homogeneous distribution of particulates on the filter surface, the shape of the filter is circular. Glass fiber filter is preferred because of its easy hand-

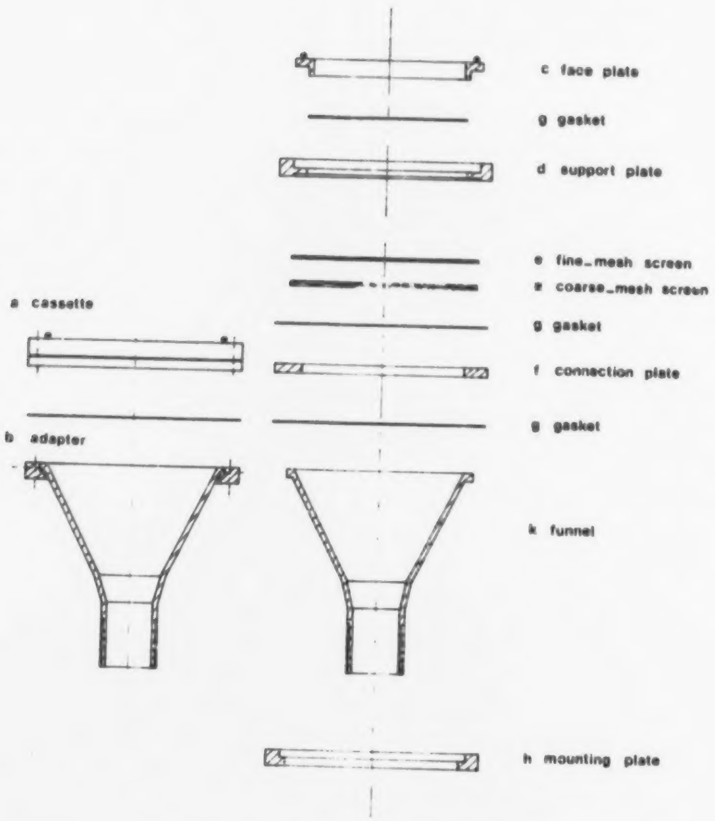


Fig. 4. Assembled and disassembled filterholder.

ling properties. The maximum diameter of circular glass fiber filters obtainable commercially, is about 15 cms. Due to possible damaging circumstances, it is preferable that the filter is stored in a cassette. In this way it is possible that only the laboratory personnel handles the filter itself. This implies that the filter holder consists of a cassette (a) and an adapter (b) which are easily connected and disconnected (figure 4). The cassette is built from a face plate (c), a support plate (d) containing stainless-steel screens as a support for the filter (e) and a connection plate (f) that is connected with the mounting plate (h) at the funnel (k). Gaskets (g)

Table I

SUMMARY OF ALL DATA

		APRIL 1971/MARCH 1972	APRIL 1972/MARCH 1973
number of data		285	298
average	(μg/m^3)	95	73
50 percentile	"	77	65
75 percentile	"	114	91
98 percentile	"	270	201
stand. deviation	"	69	56

Table II

AVERAGE CONCENTRATION PER DIRECTION OF WIND

WIND DIRECTION	APRIL 1971/MARCH 1972	APRIL 1972/MARCH 1973
N	54	42
NO	86	63
O	104	111
ZO	100	108
Z	85	91
ZW	122	97
W	71	47
NW	34	41

Table III

AVERAGE CONCENTRATION VERSUS WINDSPEED

CLASS OF WINDSPEED (M/SEC)	APRIL 1971/MARCH 1972	APRIL 1972/MARCH 1973
0 - 2	123	106
2 - 3	98	73
3 - 4	82	69
4 - 5	82	64
5 - 6	77	66
6 - 7	80	52
7 - 8	89	61
8 - 9	173	73
9 -10		83
≥10		166

The measurements with the described high volume sampler started on January 1974. From this time a sharp decrease in the copper content of the particulate matter was observed.

PERIOD	Mean copper content ($\mu g l m^3$)
January - March 1973.	0,52.
April - June 1973.	0,56.
July - September 1973.	0,65.
October - December 1973.	0,37.
January - March 1974.	0,03.

This is an indication that copper contamination from the motor does not take place.

secure a complete tightness. The cassette is made of P.V.C., the funnel, which is commercially available, is made of vulcathene. The dimensions of the ball-valves and filter holders limit the amount of air drawn through the filter to about 25 m^3/hr. To reduce time consuming calculation in the laboratory, the apparatus is adjusted to a flow of 500 m^3/day.

On determining the linear velocity of air at the entry clearance between the edge of the roof and the main housing, the advice of the U.S. Intersociety Committee of 1,13 m^3/min of air sampled through a clearance of 645 cm^2 has been followed (Sholtes [6]). In this apparatus 0,35 m^3/min is sampled through a clearance of 200 cm^2. The entry surface has been positioned horizontally to avoid catching particles generally larger than 100 μ (Jutze [5]). The whole apparatus has a housing of aluminium, to prevent corrosion at the coastal site.

3. Results

Some data of two years sampling with conventional high volume samplers are tabulated. Table I shows that for more than 75 % of the days data are available. The overall average of the particulate concentration is nearly 25 % lower in the second year.

During the first year the standard is exceeded because more than 2 % of the data are higher than 240 μg/m^3. The lower mean level in the second year is partly explained by a different frequency distribution of the winddirection and the lower level of particulates at western and southwestern winddirection (table II). The remarkable influence of windspeed on the particulate concentration is shown in table III. Both at low windspeed (0 - 2 m/sec) and at high windspeed (more than 8 m/sec) a maximum level is reached.

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ANALYTICAL STUDIES ON THE SPECIATION OF AMBIENT LEVELS OF MERCURY IN AIR

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ABSTRACT

An analysis method has been developed for the determination of several forms of mercury in air at concentrations down to 0.1 to 1 nanogram per cubic meter. Particulate mercury, elemental mercury, methylmercury(II) compounds, volatile inorganic mercuric compounds and dimethylmercury are collected from air samples onto previously blanked specific absorption tubes. These are analyzed by thermal desorption of the mercury compounds and detection of the mercury by emission spectroscopy in an electrical discharge in helium carrier gas. The analysis system has a limit of detection near 0.03 ng m^{-3} for elemental mercury, dimethylmercury and particulate mercury. The specific absorption tubes for methylmercury(II) compounds and volatile inorganic mercuric compounds have limits of detection near 0.3 ng m^{-3}. The analysis of ambient air for the several forms of mercury has been carried out over a sampling grid in the Tampa, Florida area. Diurnal variations, short term fluctuations, mercury forms in homes and buildings, and mercury evolution from lakes have also been studied.

Current results indicate that elemental mercury is the major form of mercury in air both in buildings and outside. Significant amounts of mercuric chloride-type compounds are also found. High values for mercuric chloride have occasionally

been obtained. Mercury concentrations inside places of human habitation are far greater than outside. Inorganic mercury is rapidly converted to methyl-mercury compounds and elemental mercury in the soil. Mercury in air above the Sargasso Sea was found to be generally lower in total mercury than over land areas. Because of the biological transformations, studies on the types of volatile mercury compounds present in air are needed.

1. Introduction

Mercury is perhaps the most widely distributed heavy metal pollutant due largely to the volatility of elemental mercury. Methylmercury halides, dimethylmercury and mercuric chloride are also known to be volatile.

Inorganic mercury has been shown to be converted into the more volatile methyl-mercury forms through biological activity by Imura et al [1] **and by others.**

Because of the lack of suitable analytical methods, until now no information has been available on the types of mercury compounds and their concentrations in the environment. Particulate mercury in air can be determined by activation analysis of filter pads and elemental mercury alone by direct atomic absorption if present above approximately 15 ng m^{-3}. The combination of emission spectroscopy with the use of sequential specific absorption tubes has provided the needed method for specific detection and analysis of the volatile mercury forms, and particulate, anywhere in the environment.

2. Sequential Specific Absorption Tube Sampling Sysgem

A sampling system was designed for the selective absorption of the several suspected environmental forms of mercury. Amalgamation was first studied. Silvered glass beads and gold coated glass beads were found to rapidly absorb elemental mercury. Dimethylmercury was quantitatively absorbed only on the gold beads thus providing a basis for separation of elemental mercury from dimethylmercury.

After considerable subsequent work sample tube packings were found which would specifically absorb methylmercury chloride and mercuric chloride. A tube containing silicone coated (3% SE-30) on 45/60 mesh Chromosorb-W, HCl, vapor treated, was found to retain mercuric chloride while passing methylmercury(II) chloride, elemental mercury and dimethyl-mercury. Methylmercury(II) bromide or iodide or acetate or other volatile forms are likely converted to methylmercury(II) chloride on the HCl-treated Chromosorb-W tube.

A non-siliconized Chromosorb-W column initially treated with NaOH to 0.15 milliequivalents per gram of column packing was found to quantitatively absorb methylmercury(II) chloride while quantitatively passing elemental mercury and dimethylmercury. Methylmercury(II) chloride is likely converted to the less volatile hydroxide by the alkaline column.

A glass wool filter, Gellman Instrument Co. Type A, was used as a particulate filter to complete the stack of absorption tubes. By assembling the absorption tubes in the following order and pumping air through them it was possible to separate mercury from a single air sample into five forms. Sample volumes from 0.025 to 0.200 m^3 were taken.

Glass wool filter preheated to blank	removes particulate only
Siliconized Chromosorb-W, HCl vapor treated	removes $HgCl_2$ type compounds and particulate which passes the glass wool filters
NaOH treated Chromosorb-W	removes CH_3HgCl type compounds
Silvered glass beads	removes elemental mercury
Gold coated glass beads	removes $(CH_3)_2Hg$

The efficiency of the individual tubes and the assembled stack was tested using elemental mercury, $HgCl_2$, CH_3HgCl and $(CH_3)_2Hg$ in operation under a variety of temperatures and conditions of humidity. Methylmercury (II) chloride was 83 - 100% retained on the NaOH-Chromosorb-W tube at temperatures as high as 33°C and 85% relative humidity. Mercuric chloride was 90 - 100% retained on the siliconized Chromosorb-W column up to 33°C and 85% relative humidity. Both compounds were tested for one and two-hour pumping periods. Dimethylmercury and elemental mercury were 100% absorbed on the gold and silver coated beads respectively under all conditions tested.

Careful blanking of all sample tubes was necessary to achieve good lower limits of detection for analysis.

3. Analysis System

After sampling, the stack of tubes were separated and analyzed individually for trapped mercury. Mercury was driven off from each tube by heating and passed through a quartz discharge chamber by means of He carrier gas. A direct current discharge in the chamber was used to excite the 253.65 nm Hg emission line. A conventional type recording spectrometer system described previously was used [2]. The gold and silver sections were heated directly into the discharge and de-amalgamated to give sharp mercury peaks when heated to 300 - 400°C. Chromosorb-W tubes were first heated into blanked gold coated bead transfer tubes to eliminate some volatalized interferences from air and to sharpen mercury peak signals.

The scanning capability of the system permitted verification of the presence of mercury. Calibration was accomplished by using mercury vapor. Lower limits of detection were found to be near 01 nanograms.

3. Limitations

Since no other current methods exist for the detection of specific mercury compounds in the 1-20 ng/m^3 range it was not possible to directly compare this method to another one. The identity of methylmercury(II) compounds or mercuric chloride compounds sampled from the environment depends upon comparison to known compounds (i.e. $HgCl_2$, CH_3HgCl, and $(CH_3)_2Hg$). Compounds sampled from the environment did contain mercury as determined by scanning the mercury emission line during analyses.

Methylmercury(II) type compounds and dimethylmercury far above normal concentrations were detected in air above soil treated with mercuric chloride.

H_2S and SO_2 were found to overload the Chromosorb-W (HCl) column if 2-hour pumping times were employed but were not otherwise an interference.

For the most accurate work, very careful handling of the absorption tubes is necessary to avoid contamination.

Mercury in laboratory air is a definite contamination problem.

4. Applications

The method has been used to study mercury in air in houses, aboard a ship, in school buildings and in a sampling grid in the Tampa, Florida, USA, area.

Tables I and II give data indicating some of our finding. Air over the Sargasso Sea (from shipboard analyses) contained only small amounts of elemental mercury. The larger fraction we believe was from aerosolization of sea water and is likely $HgCl_2$ type compounds. The total mercury in air found at sea compares reasonably well with the amount of mercury in the sea water evaporated into air. Sea water is on the order of 5 - 10 ppb mercury, or 5 - 10 ng/liter. If evaporated, one liter of sea water occupies 1 m^3.

Houses and buildings are obviously the greatest source of air mercury exposure to the general population. Amounts of mercury in buildings ranged from 10 to 100 times higher than mercury in ambient out-of-door air.

TABLE I Mercury in Air in Buildings and Aboard Ship (R/V Trident)

	ng/m^3 [c]					
Sample	Hg particulate	$HgCl_2$	MMC	Hg°	DMM	Total
Lecture Hall[a] (Before class)	2.9	4.2	12	310	0	367
Same Total only	-	-	-	-	-	351
Lecture Hall[a] (After class)	0	12	25	500	12	549
Same Total only	-	-	-	-	-	557
House[a]						
Bathroom	-	43	4.4	200	0	247
Bedroom	-	0	10	37	0	47
Kitchen	-	12	0	88	0	100
Living room	-	2.7	23	110	0	136
Ship (totals only)[b]						
Laboratory						21
Engine Room						51
Paint Locker						62
Faculty Office (Several) (total only)						110 - 140

[a] Out of doors total ambient Hg, 3 - 6 ng/m^3

[b] Out of doors total ambient Hg, average 7.5 ng/m^3

[c] Uncertainties in data are ± 0.3 ng/m^3 or ± 5%

TABLE II Mercury in Ambient Air

	ng/m^3					
Sample	Hg particulate	$HgCl_2$	MMC	Hg°	DMM	Total
Tampa Area (same day) Suburban Location	2	22	14	4	0	42
Bayside	3	10	54	6	3	76
Urban Downtown	12	0	3	4	1	20
Trapped air over soil treated with $HgCl_2$ (1 day after)	-	20	20	400	60	500
Trapped air over untreated soil (1 day after)	-	-	-	-	-	3 - 6
Sargasso Sea (underway)	0.1	10	0.2	0.9	0	11
Sargasso Sea (on station)	3.1	0	0.7	1.1	0	4.7
Sargasso Sea[a]	-	-	-	0.89	-	-
Sargasso Sea (underway - near waterline)		7.5, 12.0, 8.1 ng/m^3 Totals only				
(underway - top of deck)		4.0, 11, 2.4 ng/m^3 Totals only				
(on station)		4.0, 0.6 ng/m^3 Totals only				

[a] South of Bermuda

Acknowledgements

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The following individuals assisted in the development of the technique: A. D. Shumaker, J. L. Bricker, M. Ammons and C. C. Foreback.

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DISCUSSION

HARRISON (U.K.)

During air sampling, other materials may be trapped in the sampling tubes. Do these materials cause any matrix effects in the mercury discharge chamber analysis?

BRAMAN (U.S.A.)

Hydrocarbons and other organic compounds can produce a background emission (as well as the predictable band emission systems) but they become a problem only if present in exceptionally high concentrations - such as direct analysis of engine exhausts. Even then, most organic materials are driven off of the tubes prior to detection of mercury. No problems of this type arose in our environmental sampling.

BYRNE (Yugoslavia)

a) The late Dr. Williston, in his pioneering measurements of mercury in air in California, observed a peak at sunrise which he attributed to commencement of photosynthesis. Have you observed a similar effect?

b) Have you investigated, or do you have any information about the nature of "particulate mercury."

BRAMAN (U.S.A.)

a) During diurnal variation studies we have observed a delayed peak concentration several hours after sunrise.

b) We have no information on the chemical composition of our "particulate" mercury fraction. It is not any of the volatile chemical forms of mercury.

NEW TECHNIQUES FOR THE MEASUREMENT OF AIR POLLUTANTS

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ABSTRACT

Measurement research in air pollution at the National Bureau of Standards includes that applicable to ambient air, stack emissions and automotive emissions. Some of the measurement techniques developed for source emission application have been refined and made sufficiently sensitive to measure pollutant concentrations as low as background levels. The fluorescence monitor for sulfur dioxide developed by Dr. Okabe and his colleagues has been applied commercially to the problem of stack monitoring. More recently the sensitivity of the technique has been improved very substantially so that ambient air sulfur dioxide concentrations can be measured at least down to 1 part in 10^9. *This apparatus will be described and its capabilities delineated. The technique of laser magnetic resonance for the measurement of NO at concentrations typical of stack emission and auto exhaust has similarly been extended to include ambient concentrations. In addition, progress has been made in the direction of simultaneous measurement of* NO_2 *by the same technique. The most recent data obtained by the laser magnetic resonance technique will be presented. A third measurement technique developed at the National Bureau of Standards, that of dual angle, forward laser scattering for the real time measurement of particle size distribution has now been shown to be capable of revealing morphological and chemical information. The development of pyrolysis as an alternative to permeation tubes and standard gas cylinders will be described. The principle of*

the pyrolytic technique is that a thermally stable molecule which may be stored indefinitely is subjected to thermal decomposition producing a non-storable molecular species plus an exactly equal number of storable, readily measured molecular species. The pyrolytic technique has the inherent capability of tying together virtually all gaseous pollutant molecules in a single, self-consistent measurement and calibration scheme.

Finally, an absolute coulometric technique for the determination of parts per million concentrations of NO in nitrogen will be described. The technique has been used to generate confirmatory evidence for establishing the integrity of NO in nitrogen Standard Reference Materials.

1. Introduction

Air pollution measurement science is no exception to the axiom that however good things are, they can be improved. A corollary is that however bad things are they can be made worse. One job we have set out to do at the National Bureau of Standards is to improve our ability to measure ambient air pollutants and to exert every effort to avoid inventing a new, inferior measurement method. As is true with most research programs, we are not always successful and we have sometimes succeeded in inventing a square wheel. My intent here is to discuss only those aspects of our program we consider to have had a successful outcome. Because the National Bureau of Standards houses many physical measurement specialists, it was natural for us to favor the application of the more sophisticated methods of modern physics and physical chemistry in our methods-development program. Our attention has been confined for the most part to those air pollutants designated as such by the United States Environmental Protection Agency--SO_2, NO_x, CO, O_3, hydrocarbons and particulates. I will be describing only the NBS efforts.

2. Fluorescence

Until the advent of flame photometry sulfur dioxide was measured by wet chemistry. Flame photometry was highly sensitive and fast, but was unable to distinguish SO_2 from H_2S and other sulfur containing compounds. Its specificity problem was solved by incorporating gas chromatography. Unfortunately, this entailed sacrificing speed of response in the process.

The sulfur dioxide molecule had been under study in the NBS laboratory of Dr. Okabe with the objective of measuring the strength of O-S bond, when it was rediscovered that there is a very strong fluorescence excited by radiation in the region of 214 nm. In the course of the study of this fluorescence the radiative lifetime of the excited state that produces the fluorescence was found to be a few nanoseconds. The significance of this finding is that an excited SO_2 molecule has about one chance in ten of radiating its energy in the form of light before it suffers even a single debilitating collison with an air molecule. It was confirmed experimentally, that 10-15 percent of the excited states of SO_2 radiate light (fluoresce) at atmospheric pressure. The basis for the design of a radically new instrument for measuring sulfur dioxide had been discovered. Once the basic discovery was made, it was possible to design an extremely simple apparatus of a design shown in figure 1.

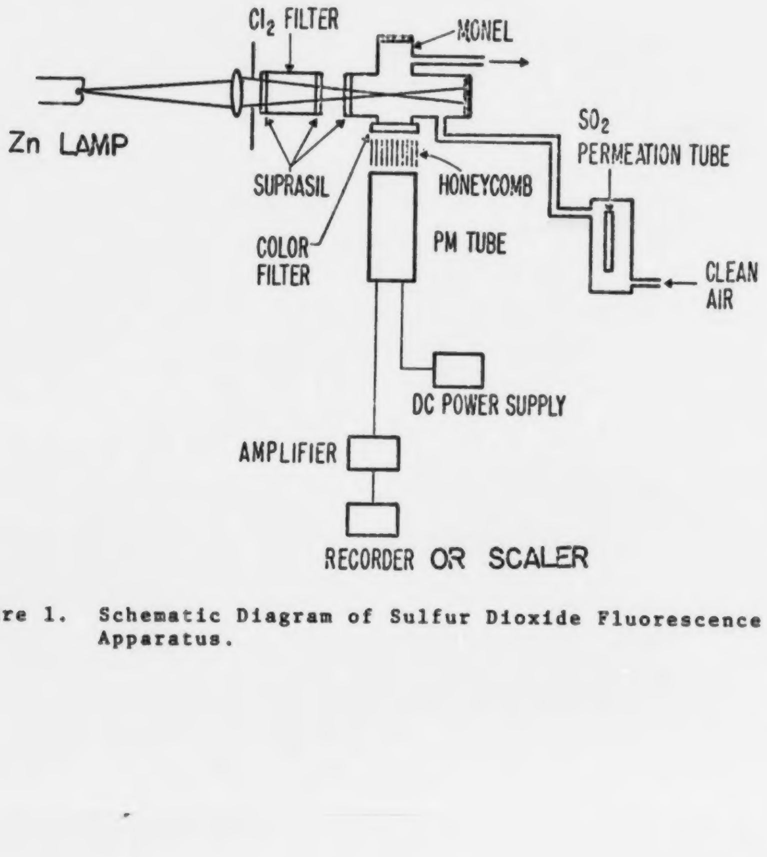


Figure 1. Schematic Diagram of Sulfur Dioxide Fluorescence Apparatus.

A chlorine filter transmits 90 percent of the Zn (214 nm) line and the Cd (229 nm) line while removing the emission lines in the light source from 270 to 390 nm. The color filter transmits the SO_2 fluorescence and rejects the 214 nm and 229 nm lines of the light sources Zn and Cd, respectively.

The performance of this apparatus or samples of air containing sulfur dioxide at concentrations determined by means of certified NBS sulfur dioxide permeation tubes is shown in Figures 2 and 3 and shows a linear signal from 0.2 to 200 ppm with the Zn lamp and to considerably higher concentrations using the Cd lamp. Recent results indicate that this linearity is maintained at least down to 10 parts per billion.

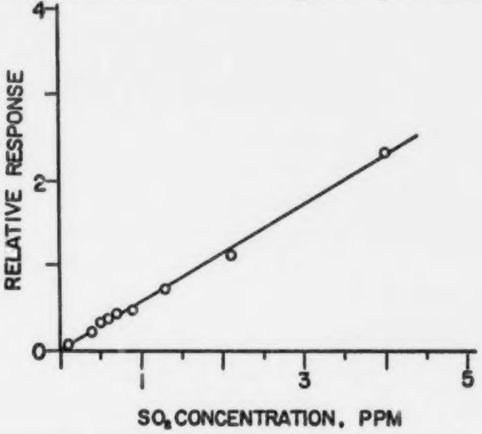


Figure 2. Response of Sulfur Dioxide Fluorescence Monitor at Low Concentrations.

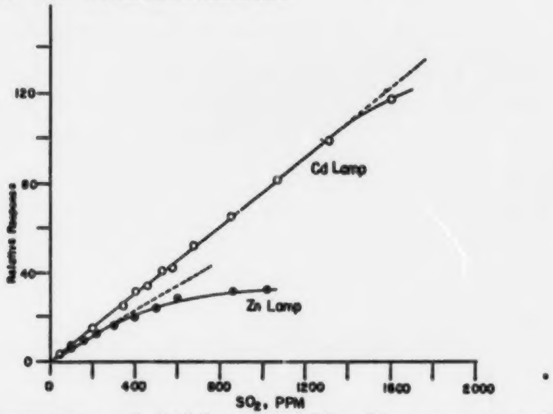


Figure 3. Response of Sulfur Dioxide Fluorescence Monitor at High Concentrations.

An extension of the fluorescence technique using laser excitation is being explored. A potassium pentaborate crystal is being used to double a tunable dye laser down to 217 nm. Early results already show an ability to measure SO_2 by laser induced fluorescence at 1 ppb essentially instantaneously. Remote sensing of stack emissions is one objective of this research. However, the main purpose of the research is to measure ambient SO_2 instantaneously at 1 ppb.

It has been found that the 214 nm Zn line also excites the fluorescence of NO in the gamma system, $A^2\Sigma^+ \longrightarrow X^2\Pi$. The radiative lifetime of the $A^2\Sigma^+$ state of NO is 2.2×10^{-7} seconds and is readily quenched by oxygen but not by nitrogen. Therefore, NO in N_2 can be measured by fluorescence down to a few ppm using a 25-second integration time. The number of counts has been found to be proportional to the concentration of NO in nitrogen from one ppm to a few hundred parts per million. The method is currently being explored as a means to monitor routinely concentrations of NO in N_2 in the NBS automotive exhaust emission Standard Reference Material.

3. Zeeman Spectroscopy

Two closely related techniques have been used at the National Bureau of Standards to measure paramagnetic molecules. Laser Magnetic Resonance, first used in Dr. Evenson's laboratory to study rotational Zeeman spectra of O_2 has now been extended to the free radicals NO, NO_2, OH, CH, HO_2, and HCO. The method is based on the property of a paramagnetic molecule that its rotational energy levels are split into (2J + 1) sublevels when a magnetic field is applied. A particular wavelength of a water vapor laser (78.4, 79.1 or 118.6 μm) is incident on a cell containing the paramagnetic molecule which has a rotational transition sufficiently close to the laser wavelength that absorption can be made to occur by application of a magnetic field to the cell. In the case of the OH radical, the $J = 5/2 \longleftarrow J = 3/2$ rotational transition is in near coincidence with the laser radiation. Four transitions in which $\Delta M = 0$, are the allowed transitions in which the laser electric field is parallel to the applied magnetic field. Abosprtion is measured by ac modulation of the magnetic field and phase sensitive detection of the laser signal. The technique is capable of measuring 2 x 10^8 molecules of OH/cm^3. The kinetics of reactions of OH with CO and with NO and NO_2 have been studied using this technique. Zeeman-Vibrational Spectroscopy has been employed by Maki, Kaldor, and Olson in a similar way to the measurement of NO. In this case the X $^2\Pi 3/2$ state of NO has a near coincidence in its J = 5/2 ← 3/2, ν = 1 ← 0 transition at 1884.32 cm^{-1} with a CO laser line (ν = 9 → 8)P(13) at 1884.37 cm^{-1}. As shown in figure 4, very modest magnetic fields are able to

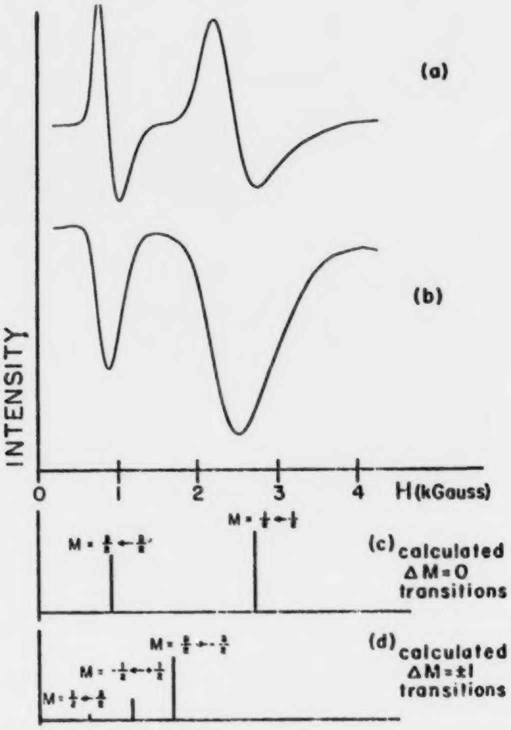


Figure 4. Response of Zeeman Vibrational Spectroscopy Apparatus to Nitri- Oxide.

bring the vibrational transitions of NO into coincidence with the CO laser transition. In a collaborative effort with Professor A. Cabana, Sherbrooke University, the ν_3 band of the NO_2 spectrum is being measured in high resolution and is being analyzed at NBS. It is expected that this will result eventually in an apparatus capable of simultaneous measurement of NO and NO_2 by Zeeman Spectroscopy.

4. Stark Spectroscopy

A Stark cell has been built in Deslattes' laboratory and will shortly address itself to the question of whether advantage can be taken of the Stark effect, modulation of the electric field and phase sensitive detection of absorption by such pollutant molecules as formaldehyde, hydrogen sulfide, ozone, etc.

5. Piezoelectric Sensors

The change in the fundamental frequency of a piezoelectric crystal is proportional to the increase of mass per unit area when a pollutant is deposited on the face of the crystal. Advantage has been taken by Scheide of this property of piezoelectric crystals by evaporating a thin film of gold onto the crystal and measuring the increase in mass resulting from the interaction of mercury with gold. The detection limit is 10^{-12} grams and concentrations of mercury in air are readily measured at one part in 10^{10}.

6. Coulometric Measurement of NO

In order to obtain confirmatory evidence for the composition of NO in N_2 Standard Reference Materials in the parts per million range, a method independent of gravimetry is required. Coulometry represents such an independent method which has been developed by Marinenko. The chemical scheme employed in the analysis is as follows:

1. $2NO + 5H_2 \xrightarrow{\text{Catalyst}} 2NH_3 + 2H_2O$

$2NO_2 + 7H_2 \xrightarrow{\text{Catalyst}} 2NH_3 + 4H_2O$

2. $NH_3 + H_2O \longrightarrow (NH_4OH) \rightleftarrows NH_4^+ + OH^-$

The electrochemical measurement scheme is based on the anodic reaction

3. $2H_2O \longrightarrow O_2 + 4H^+ + 4e.$

The final stoichometric reaction is

4. $H^+ + OH^- \longrightarrow H_2O$

i.e. neutralization of ammonium hydroxide with electrogenerated sulfuric acid.

All samples in the 100% to 0.1% NO concentration range were analyzed by injection of a known volume of gas (25 cc) into the H_2 stream and titration of the absorbed ammonia. Below 0.1% NO, gas samples were continuously injected at a known rate and the flux balance method of analysis was employed. The results of analysis of known mixtures are summarized graphically in Figure 5.

The data obtained for $NO-N_2$ mixtures, covering six orders of magnitude concentration range, confirm absence of any systematic measurement error (bias). Work is proceeding in cooperation with the gravimetric preparation group in an effort to resolve some observed descrepancies.

7. Particle Size by Light Scattering

An instrument has been designed, built, calibrated and tested in Gravatt's laboratory which sizes particulates by the intensity ratio technique. The basic concept involves the simultaneous measurement of the intensity of light scattered by a single particle at two small scattering angles. The ratio of the two intensities is a direct measure of the size and is fairly independent of the index of refraction of the particle. The optical system consists of an argon ion laser

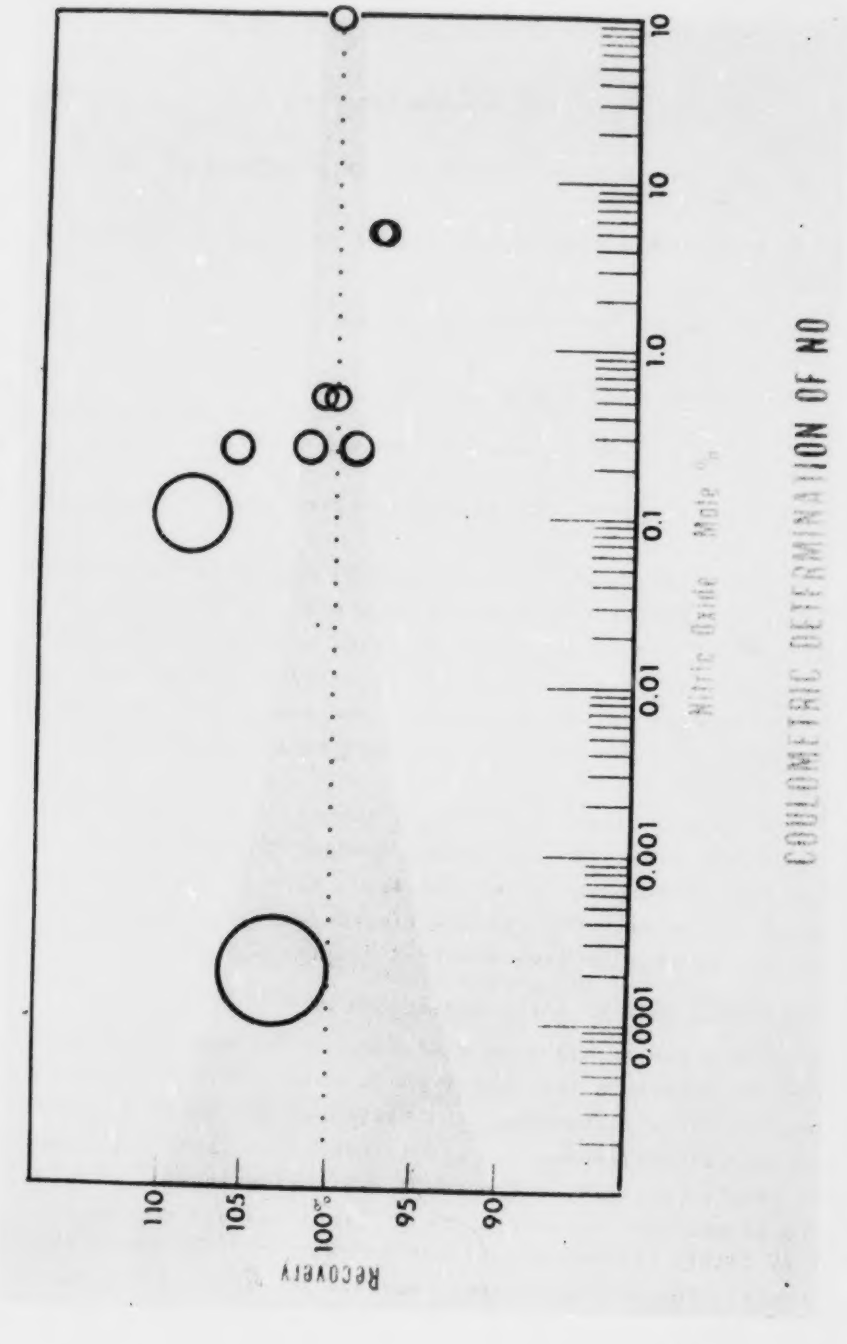


Figure 5. Efficiency of Recovery of Nitric Oxide From Known Mixtures of Nitric Oxide in Nitrogen.

source and an annular iris-fiber optic scattered light detector. The maximum count rate of the system is 20,000 particles/sec and the diameter range covered is 0.2 μm to 4 μm. For the scattering angles of 10°and 5° this technique can size particles in the 0.2 μm to 4 μm range with an error no greater than ±15% for all possible materials in air. In addition, optimum angular ratios and apertures have been determined for a wide range of sizes.

The conversion of the analog ratio light scattering instrument to a digital instrument with computer data acquisition and analysis has been completed.

A very simple method for distinguishing between optically absorbing particles, e.g., carbon and metals, and non-absorbing particles was found from theoretical studies. This involves a measurement of the absolute scattered intensity over the angular range 30° to 70°.

A preliminary theoretical study of the depolarized light scattering by long rods has been performed. It appears that a measurement of the ratio I (depolarized)/I polarized would serve as a way of detecting asbestos particles.

Instrumentation for field use has been developed by Greenough for the Environmental Protection Agency to determine the size of particles in the 0.1 to 5 micrometer diameter range.

8. Calibration Standards by Thermal Decomposition

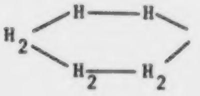
The aim of this project is to investigate the possibility of generating dilute, known quantities of pollutant gases through the thermal decomposition of appropriate "parent" compounds. Such an *in situ* procedure provides a simple solution to the difficult problem of preserving the integrity of dilute samples of pollutant gases prepared in the usual static manner. Furthermore, through the proper selection of the parent molecule, such a procedure may be easily calibrated. That is, for the reaction A (parent)→B (pollutant) + C, where C is a more stable and easily calibrated species, then a determination of the concentration of C will fix the value for B. Finally, by controlling the concentration of the "parent" molecule and/or the extent of decomposition, any concentration of pollutant can be readily produced. Overall, the present procedure calls for a minimal amount of experimental skill and is thus ideal for incorporation into test instruments and routine field usage.

The experimental procedure is to use as the parent compound a molecule which decomposes into the desired components via a molecular mechanism. It is particularly important that there is no possibility of free radical induced decomposition since such systems may not be reproducible. The selected compound is then pyrolyzed in a gold tube reactor and the requirements are that only the expected products be produced and in the proper stoichiometric proportions.

A demonstration of the feasibility of this method as a means of generating formaldehyde, acetaldehyde and acrolein has been completed in Wing Tsang's laboratory. The relevant reactions are

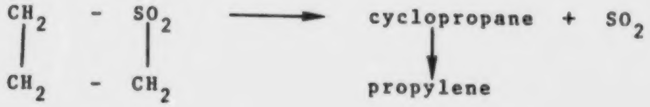
$$H_2C{=}C{-}CH_2CH_2OH \longrightarrow \text{isobutene} + HCHO$$

$$H_2C{=}CH{-}CH_2CH(OH)\ CH_3 \longrightarrow \text{propylene} + CH_3CHO$$

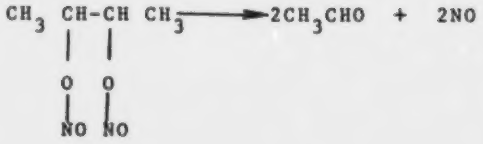
and  $\longrightarrow$ ethylene + $H_2C{=}CHCHO$ (acrolein)

The key points to be noted are the equality (on a mole basis) of the olefins and aldephydes formed, the great variation available in the concentration of pollutant in the gas delivered to the detector and the wide range of temperatures possible. It is expected that the generation of organic acids, alcohols, ketones and hydrogen halides will proceed with equal facility.

Two substances that appear to behave in the required manner for generation of SO_2 and NO are shown in the following reactions.



and



$$\mathrm{CH_3\,CH(ONO){-}CH(ONO)\,CH_3 \longrightarrow 2CH_3CHO + 2NO}$$

It should be noted that the trimethylene sulfur dioxide system has characteristics which make it ideal for present applications. For example, at 0°C it is a solid with a vapor pressure of the order of 0.03 Pa (0.2 microns). Thus, with a carrier gas at 1 atm and with complete reactions (>800°C) one obtains SO_2 at the .3 ppm level. At 70°C it is a liquid and its vapor pressure is such that with 1 atm of the carrier gas one obtains ~300 ppm samples.

I have given you a few examples of what we at NBS regard as new techniques in measuring air pollutants. Obviously these examples represent only a small part of the whole of new-techniques research. Nevertheless, they represent our best efforts and we believe they are not insignificant in the total picture.

DISCUSSION

CERQUIGLINI (Italy)

Calibration of monitoring systems in automatic networks with transmission of data to a central data collection operative unit, made by current dynamic methods, is quite expensive.

Do you think that in the future the thermal decomposition method of calibration could be adopted to this use?

McNESBY (U.S.A.)

Yes. This is exactly the point of developing the thermal reactor. The same reactor can be used to generate known concentrations of a number of pollutants.

SPECIFIC HYDROCARBON MONITORING AT LOW CONCENTRATIONS

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ABSTRACT

The extensive use of hydrocarbons and the wide variation in their physiological effects necessitates a more detailed study of the hydrocarbon composition of the atmosphere. Total hydrocarbon measurements, the method used extensively at present, give no indication of the levels of individual potentially dangerous compounds present in the urban atmosphere.

One of the major problems involved in studying the medical effects of individual hydrocarbon air pollutants is that of sampling, at street air concentrations, in such a way as to render subsequent separation and analysis possible. If, for instance, adsorption tubes containing standard chromatographic materials are used at sub-ambient temperatures, difficulties arise with water condensation. In addition the amounts of volatile materials collected are limited by the relatively low retention volumes involved. These problems of sampling and analysis can be overcome by use of the "Timed Elution Procedure". Here the hydrocarbons are sampled quantitatively at ambient temperatures by adsorption onto Chromosorb 102. The sample tubes are then heated to 130°C and a proportion of the collected material is eluted via a sampling valve onto the main chromatographic column for analysis. For a given sampling tube, the proportion of each species eluted in this timed-interval is a linear function of the total amount collected allowing both quantitative analysis and, if necessary, GC/MS identification of the species present.

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This technique allows, for example, street air benzene levels to be readily assessed. It is also important in that it is within the C_6 - C_{10} *hydrocarbon range that petrol and diesel exhaust emissions differ most markedly. These hydrocarbons can be readily sampled and separated by this method and their relative contributions to the street air hydrocarbon levels may be measured. Very low levels of alkylbenzenes, indans and tetralins, which contribute to exhaust odour can also be estimated.*

In the U.K., where the tendency towards photochemical smog formation is not very great, the main problem caused by vehicle exhaust emissions is that of odour nuisance with its possible health hazard. For this reason considerable effort has been directed towards identifying the individual compounds present in exhaust emissions, with particular emphasis being given to diesel exhausts.

No single component is responsible for exhaust odour and complex synergisms undoubtedly occur. One group of exhaust components, the unsaturated hydrocarbons, arising from the original fuel or formed as pyrolysis products in the combustion process, are undoubtedly responsible for a considerable part of the odour. Other possible odourants include oxygenates, and compounds of sulphur and nitrogen. The former occur at levels at least an order of magnitude lower than the aromatics (A.D. Little,[1]) but may possibly contribute to exhaust odour to an equivalent extent. The low molecular weight aldehydes such as formaldehyde, acrolein and crotonaldehyde, once suspected of being prominent odourants, are no longer considered to be important (Vogh.[2]). At the odour threshold of diesel exhaust in air, (a dilution factor of about two hundred) levels of these species are typically only a tenth of their odour thresholds (Table 1) (Vogh [2].).

TABLE 1. Odour thresholds of possible exhaust odourents
(after Leonardos, Kendall and Barnard 8 , Gerarde 3)

Chemical	Odour threshold ppm
Acetaldehyde	0.21
Acetone	100.00
Acrolein	0.21
Benzene	4.68
Cyclohexane	300.00
p-Cresol	0.001
Dimethylsulphide	0.001
Formaldehyde	1.00
Phenol	0.047
Styrene	0.047
Toluene	2.14
o-Xylene	0.17
p-Xylene	0.47

Organic sulphur compounds have been suggested as possible exhaust odourants due to their very low odour threshold levels in air (approx 0.001 ppm Table 1.). Even if the total exhaust hydrocarbon fraction consisted of entirely unchanged fuel, then individual sulphur species would only just exceed their threshold odour levels in the diluted exhaust gas. However this is far from being the case in that the most reactive species present in the fuels and presumably the odourous sulphur compounds fall into this category, are readily oxidised or otherwise modified. Further it has been suggested that with modern fuels of low sulphur content, the final combustion product sulphur dioxide contributes little to the exhaust odour (Vogh[2].). **Nitrogen** dioxide is thought to be the only nitrogen compound that contributes strongly to the exhaust odour of a diesel engine, but only in the idling mode (Vogh[2].).

The spectrum of hydrocarbons emitted from a source can be related to the type of odour produced. Thus the major differences in exhaust odour note between petrol, jet aircraft and diesel emissions broadly parallel the fuel composition, which in turn determines the reactive hydrocarbon and oxygenate emissions (Table 2.). For petrol exhausts the main aromatic species are

TABLE 2

The Relative Contributions of Various Structure Types to the Total Exhaust Aromatic Fraction

	Emission Source		
Structure Type	**Petrol**	**Aircraft (JP4)**	**Diesel**
C_6 - C_9 **Benzenoid***	69%	49%	38%
o-Xylene + remaining Benzenoid	29%	41%	44%
Indane.	1.2	5.	9.
Naphthalenes	0.7	5.	9.

***Benzene, toluene, m, p-xylenes, ethylbenzene, ethyltoluenes.**

Engines run at fast idle, under no-load conditions.

simple alkylbenzenes, which with the exception of o-xylene are sweet in odour. Other materials of increased complexity arising from increased ring substitution or chain branching cause the odour to become more acrid (Gerarde[3].). These are more prevalent in jet aircraft and diesel exhausts. In addition indans and other mixed cyclic species also have kerosine-like odours. Thus where procedures are available for the collection of hydrocarbons from street air, the contribution of aromatic species to the 'oily-kerosine' odour note can readily be assessed.

The most abundant hydrocarbon species found in street air, apart from the simple alkanes, are the early members of the aromatic series. Toluene is present to the greatest extent in the street air of the U.K. and North America (Perry and Twibell [4]., Pilar and Graydon [5].), where it occurs at levels slightly over twice those of benzene. Total levels of C_8H_{10} isomers roughly equal the toluene level. The situation is apparently different in Switzerland where benzene appears to be the most abundant (Grob & Grob [6].). This may reflect differences in petrol composition, petrol exhaust being the major contributor of these species.

The basic C_6-C_{12} hydrocarbon composition of the urban atmosphere reflects the composition and densities of the traffic in the street, and could be used as an indication of the odour nuisance and potential health hazards.

Sample Collection. Procedure for Hydrocarbon Monitoring

Modern porous polymeric adsorbants have large retention volumes for volatile organic species at ambient temperature. Water is not readily retained and the sample, following collection, may be stored for several weeks.

Desorption of this sample prior to analysis can be a problem. Although solvent extraction may be used for this purpose it results in considerable sample dilution in addition to the loss of the most volatile materials.

Furthermore, if gas chromatography linked to mass spectrometry is to be used for identification, the limiting source pressure precludes the identification of species eluted with, or close to, the main solvent peak. A Timed Elution procedure was therefore devised to overcome these problems (Perry and Twibell [4] , [7] .).

The sample is collected in short lengths of 6mm O.D. stainless steel tubes packed with 0.3g of Chromosorb 102. The tubes are returned to the laboratory and connected into the gas sampling valve system depicted in Figure 1, which is then heated to 130°C. At this temperature equilibrium distributions are established for each species between the adsorbant and the gas present in the void spaces. The relative amount of a specific hydrocarbon in the vapour phase, at a given temperature, thus depends upon the volatility of the species as well as upon the space available. This in turn is determined by the tightness of the adsorbant packing and the volume of any associated pipework. A timed valve actuator switches the gas chromatograph carrier gas supply through the tubes for a five second period, completely eluting the vapour phase material onto the chromatography column. This ensures that the organic materials are in a sufficiently small plug to be resolved by the column. Broad classification of the eluted species was carried out using a Hewlett-Packard 5930A mass spectrometer fitted with a gas chromatographic inlet and linked to the H.P. 5932A data system.

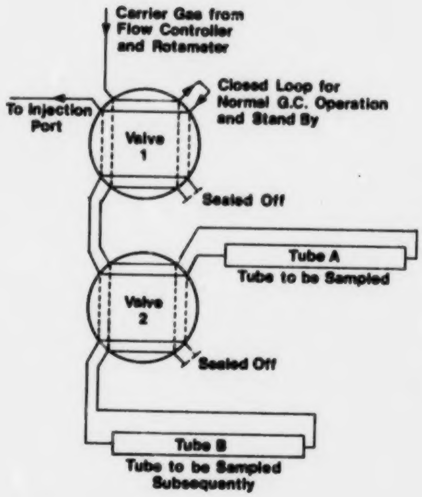

Figure 1. Timed Elution Gas Sampling Valve Assembly, Schematic.

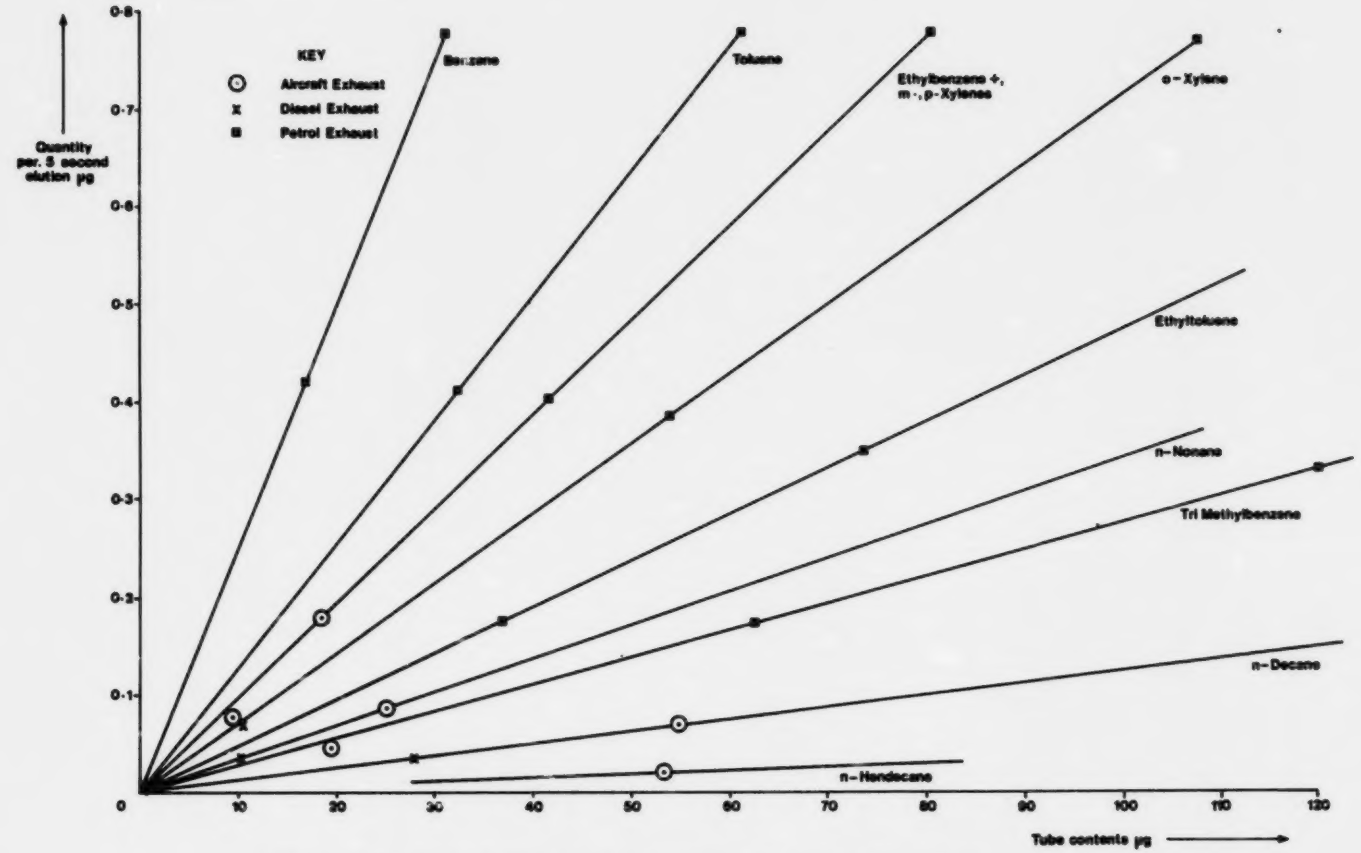

Figure 2. Typical Elution Gradients of Various Hydrocarbons.

Hydrocarbon Levels in Urban Air

Kerbside street air analyses at typical sites are given in Table 3.

TABLE 3

Typical Street Air Hydrocarbon Levels

	Pinstone St. Sheffield		Exhibition Rd. London		Mobile Sampling M4 Motorway	
HYDROCARBONS	μgm^{-3}	ppb	μgm^{-3}	ppb	μgm^{-3}	ppb
Benzene	270	85	576	179	1100	344
Toluene	550	146	1210	322	2500	665
Ethylbenzene)					400	92
)	400	92	850	192		
m,pXylenes)					2700	624
o-Xylene	184	43	290	67	1060	245
p-Ethyltoluene	270	55	280	57	920	188
Trimethylbenzenes	112	23	150	31	840	171
n-Decane	40	7	60	10	1060	182

(Notes to Table 3)

Pinstone Street is a major shopping street in Sheffield, heavily contained by large buildings. At the time of sampling traffic flows were 1310 vehicles per hour, 19% of which were diesel fueled. There was a fresh blustery wind blowing along the street direction.

Exhibition Road is a wide dual carriageway with tall buildings either side. At the time of sampling (in the central reservation) there was no wind, hot dry weather prevailing. Traffic flows were 1922 vehicles per hour, with a 22% diesel composition.

Mobile sampling on the M4 Motorway was performed in a platoon travelling at 45-50 mph, the sampling vehicle maintaining the recommended braking distance. There was a slight cross wind. Sample inlet was positioned adjacent to the interior ventilation intake on the vehicle bonnet.

Comparison of the individual aromatic hydrocarbon levels obtained at the Sheffield site, with their odour threshold values, (Table 2) indicates that the xylenes were present at about a quarter of their

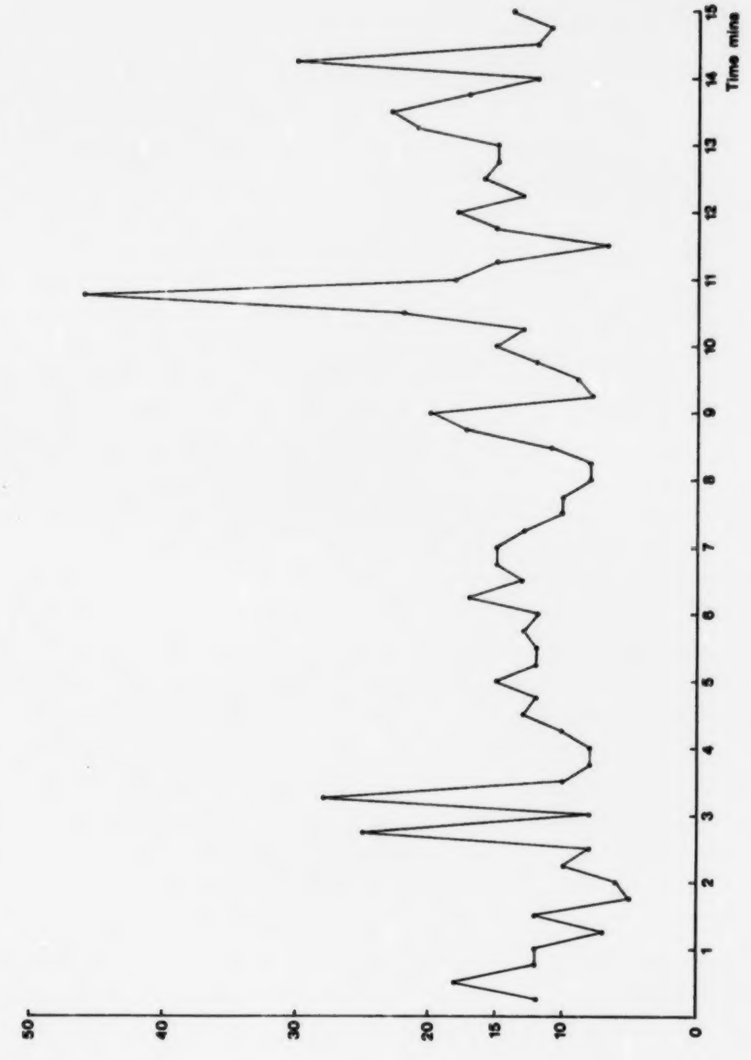

Figure 3. Fluctuations in Kerbside Carbon Monoxide Levels During Hydrocarbon Sampling at Pinstone Street, Sheffield.

TABLE 4

BASINGSTOKE INCINERATOR EMISSIONS

POLLUTANT	START-UP PROCEDURE			NORMAL OPERATION			SHUTDOWN	
	Ignition	warm-up		Primary air only		Primary + 35% 2ndary		
	21/11/73	21/11/73		20/11/73		22/11/73	29/11/73	
BENZENE µg/m^3	190	350	230	300	280	330	340	260
TOLUENE µg/m^3	820	550	490	450	280	700	70	100

odour threshold levels. Olfactory response is extremely rapid and ideally fluctuations should be monitored on a much shorter scale. This at present is not possible when monitoring individual hydrocarbons at these levels. However some indication of probable fluctuation can be obtained from the carbon monoxide levels which were monitored simultaneously (Fig.3). Here peak values of up to four times the mean were found at the Sheffield site. Assuming good correlation between carbon monoxide and the hydrocarbons it is apparent that the levels of aromatic species peak over their threshold levels. Fluctuations in kerbside levels are undoubtedly caused by turbulent mixing processes diluting the exhaust, rather than by diffusion hence the lower diffusion rates of aromatic species relative to carbon monoxide are of minor importance. Similatly the mean levels found in Exhibition Rd., London, were higher and thus it is to be expected that odour thresholds were exceeded for a greater proportion of the sampling time.

Municipal refuse incinerator emissions

The levels of aromatic hydrocarbons emitted by a modern municipal waste incinerator were examined. The only species found to any appreciable extent were benzene and toluene, other aromatics being at very low levels. Sampling was performed in the stack base after electrostatic dust precipation and water scrubbing. The levels found (Table 4) were no greater than those found in a heavily trafficked street. There thus appears to be no reason for undue concern about benzene emissions from incinerators of this design.

It should be noted that although the benzene level was almost independent of incinerator mode, toluene varied greatly. We believe that increased adsorption of toluene by particulates must occur as the system cools, the toluene being re-emitted during warm-up. Secondary air may cause premature flame quenching.

Hydrocarbon levels inside vehicles

The levels of aromatic hydrocarbons in the passenger air-intake of a car were examined. The sample was taken at the bonnet air-intake of a car forming part of a traffic platoon travelling along the M4 motorway. It is apparent from the results (Table 3) that the levels of some aromatic species are permanently in excess of their odour thresholds, although olfactory fatigue will obviously occur.

Possibility of Health Hazards

Of the aromatic species investigated in street air only, benzene has been linked with definite health hazards. It is a suspected carcinogen and is known to accumulate in bone marrow. However levels of benzene occurring in street air are about two order of magnitude lower than those recommended as maximum allowable concentrations over an 8 hour period, in industrial establishments. Even the highest level measured inside the vehicle moving in a traffic stream was only 3.5% of the accepted industrial level. Exposure to benzene as an air pollutant from traffic does not at present appear to be a significant health hazard, although nothing is known of the effects of long term exposure to these levels. In addition the presence of other exhaust derived materials may exacerbate the toxic effects.

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DISCUSSION

MERIAN (Switzerland)

I'm interested in the environmental pollution by hydrocarbons and its relation to ecotoxicology (see Chimia 28 (May 1974) and paper of 2 July 1974 at the Environmental Medicine and Biology Congress, Paris). In your Table 3 you mention concentrations of 0,3 to 1,1 mg Benzene/m^3, of 0,6 to 2,5 mg Toluene/m^3 and of 0,6 to 3,8 mg Xylenes/Ethylbenzene/m^3 in Sheffield and London.

A.P. Altshuller, W.A. Lonneman and K. Grob found only about 0,04 mg Benzene/m^3, 0,06 to 0,15 mg Toluene/m^3 and 0,02 to 0,15 mg Xylenes/m^3 in Los Angeles Azusa, New York Manhattan, New York Lincoln Tunnel and in Zurich. G. Guiochon found even much lower concentrations in Paris.

Do you have an explanation why you found about 10 times highe concentrations in the UK.

TWIBELL (U.K.)

I would like to emphasise that we were looking for extreme cases and the street air samples were taken at the kerbside at a height of only 5 feet. We were primarily interested in the effects of aromatic hydrocarbons on the pedestrians in the street, and therefore we sampled at nose level. Other authors tend to be rather vague about their sampling site details, but Grob and Grob (J. Chromatogr. 62 1-13 (1971)) state that they found 54 ppb. benzene and 39 ppb toluene at a site in their university campus 300 metres from the nearest road. I therefore believe that our highest kerbside levels of 179 ppb benzene and 322 ppb. toluene are not at all out of agreement.

The motorway samples are higher as the air entering a vehicle obviously contains a poorly diluted portion of the exhaust of the vehicles in front. Sampling was undertaken in the air intake (interior ventilation system) of a vehicle moving rapidly in heavy traffic on an urban motorway. The intention was to investigate the levels of aromatic species which motorists may be subjected to under these conditions. The relatively high level of decane reflects the proportion of diesel fueled vehicles overtaken during the sampling.

BRAMAN (U.S.A.)

Have you noticed any decomposition of the chromasorb 1o2 during heating?

TWIBELL (U.K.)

The temperature of desorption was 130°C. At this temperature no decomposition of the chromosorb occured. Preliminary experiments showed very heavy contamination by styrene and other species. A ten day soxhlet extraction using five changes of cyclohexane proved to be an adequate clean-up procedure. No further problems were encountered. The recommended temperature limit for this material is 250°C.

BARRATT (U.K.)

We have considered using a trapping system for the analysis of surgical environments where there is assumed to be harmful pollution by volatile anaesthetic agents. Can you describe how you have evaluated the performance of your analytical system and how the calibration has been carried out?

TWIBELL (U.K.)

The collection efficiency of the system was evaluated during tube calibration, by means of a gas sampling value loop situated in the line after the sampler. Periodic analyses of the exit cases were made in order to check that the retention volumes of the species under observation had not been exceeded. At the sampling rates involved (~0.5l/min.) aromatic species were completely retained up to approaching their retention volumes (9 litres could be sampled before benzene began to break through).

Tube calibrations were carried out using a range of dilutions of auto exhausts, down to the limit of quantitative G.C. Detectio Although held in plastic bags, bag losses were overcome by analysing the gases at the sampling tube entry, after the particulate filter. Several analyses were performed to check homogeneity of the samples mixture. Rotameters and wet gasmeters were used to calculate the total volume hence total quantities absorbed. Calculation of total amounts collected at lower concentrations was by several extractions of the packing with chlorinated solvents and G.C. analysis of solutions, after timed elution.

The results of the third elution were used to calibrate the technique, the first elution never being representative.

A SYSTEM FOR THE RAPID IDENTIFICATION OF TOXIC ORGANIC POLLUTANTS IN WATER

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ABSTRACT

A system has been developed that will identify, within a few hours, any of eight thousand organic compounds in water at concentrations as low as 0.01 µg per liter. A one-liter sample of water is extracted with an appropriate, water-immiscible, organic solvent. After the extract is concentrated to 100 to 1,000 microliters, a portion is injected into a gas chromatograph coupled to a computer-controlled mass spectrometer. As separated compounds pass through the mass spectrometer, spectra are recorded on magnetic disks frequently enough to obtain several spectra for each compound.

Compounds are identified from their mass spectra by computerized spectra matching. A central computer library contains spectra for eight thousand compounds. The computer selects and lists the compounds whose spectra are similar to that of the unknown, in order of their degree of similarity. The computer also assigns a numerical value for the similarity between the unknown and each listed spectrum from the library, giving the analyst a high degree of confidence in the reliability of the identification. Further confirmation of the compound's identity can be made by comparing gas chromatograph retention times and by obtaining infrared absorption spectra or chemical ionization mass spectra.

With approximately twenty-five mass spectrometers located throughout the United States, the laboratories of the Environmental Protection Agency can contribute to the continuous recording of the geographic frequency distribution of toxic pollutants. When a spectrum is referred to the central computer together with the location of the sampling site from which the corresponding compound was obtained, the computer automatically records the location for each identified compound.

The library of spectra is being upgraded continually by carefully elucidating the structures of previously unidentified organic water pollutants. High-resolution mass spectra, infrared spectra and nuclear magnetic resonance spectra are used in the initial identification of pollutants whose spectra are not in the computer library. Once their identities are certain, the spectra are added to the library.

The computer usually identifies over half of the compounds in samples from a wide variety of industrial waste effluents. In many cases the total cost for an identification is less than ten dollars.

1. Introduction

In any study of the relationship between observed human health effects and exposure to environmental pollutants, one must be certain that the effects he observes result from the cause that he attributes them to. Therefore he must have knowledge of all components in the systems he is studying, not just those whose effects he is concerned with in the study.

During the past few decades tens of thousands of organic chemicals have been introduced into the aquatic environment as a result of the chemical technology explosion. With so many organic compounds to consider in samples of water from streams that receive industrial and municipal waste effluents, agricultural run-off and atmospheric fall-out, it is mandatory that the water be analyzed qualitatively for the presence of specific toxic pollutants. The system described in the Summary to this paper (Webb et. al. (1)) should prove to be a powerful tool in the evaluation of health effects, as it has already proven to be in studying ecological effects in the aquatic environment (Alford (2)).

2. Identification of Carcinogens

To demonstrate the applicability of the system to the identification of compounds of significance to health-effect studies, a synthetic sample was analyzed. Four carcinogens (selected from the OSHA list of carcinogens, July 27, 1973) were added to a sample of Oconee River water to provide a concentration of approximately 50 μg/l for each carcinogen. The river was sampled a few hundred feet downstream from a municipal sewage effluent. The stream, therefore, was typical of those that must be considered in assessing potential health effects of municipal water supplies — particularly those in which sewage may be recycled to the supply.

The sample was extracted with methylene chloride, concentrated by evaporation, and injected into a Varian Model 1400 gas chromatograph equipped with a 6 ft., 0.25 in. (O.D.) column, packed with 3% SE 30 on Gas Chrom Q. The effluent from the gas chromatograph flowed directly into a Finnigan Model 1015 quadrupole mass spectrometer with a Systems Industries data system.

Figure 1, the resulting computer-reconstructed gas chromatograph (RGC), shows the four separated compounds that were subsequently identified as the

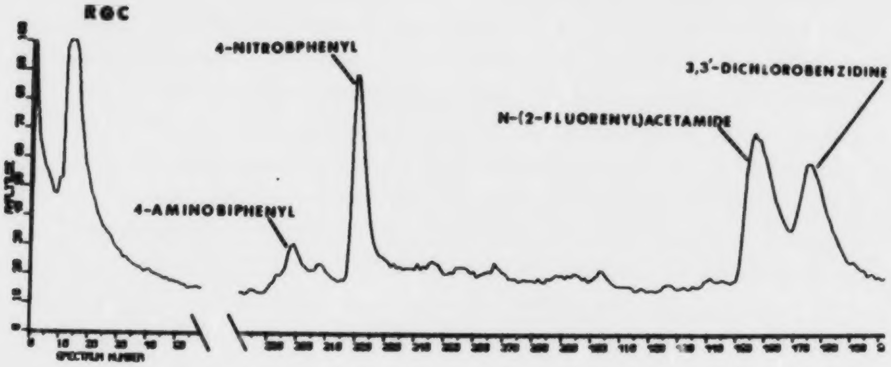

Figure 1 : Computer reconstructed gas chromatograph.

carcinogens added to the sample. Mass spectrum number 320 was selected as the optimum spectrum for identifying 4-nitrobiphenyl. The computer was instructed to plot spectrum number 320 with spectrum number 317 subtracted (to eliminate background ion fragments). The computer-purified spectrum is shown in figure 2. Mass 199 represents the singly-charged, unfragmented molecular ion for nitrobiphenyl.

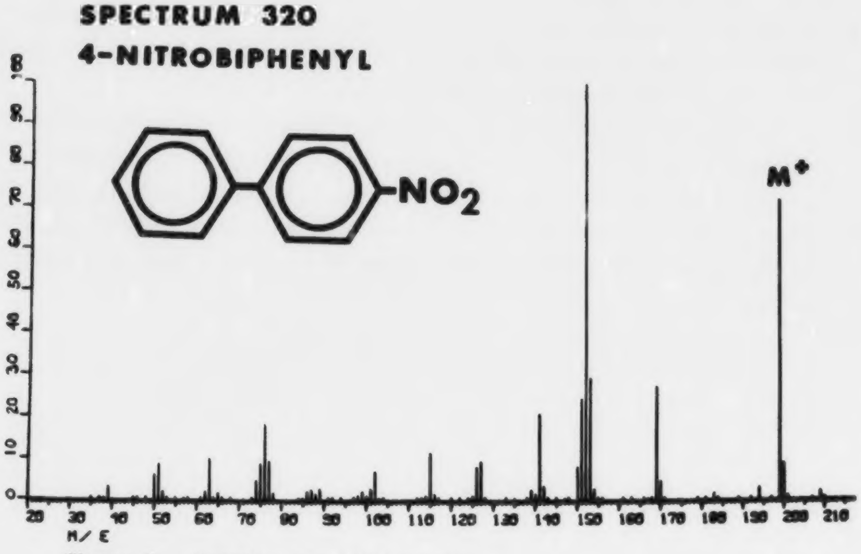

Figure 2 : Computer purified spectrum

A digital description of this spectrum (containing the relative amplitudes for significant mass-to-charge ratios) was transmitted to a second computer for comparing with the spectra of 8,000 compounds in the computer's library. The computer located 8 spectra that were similar to the spectrum representing the unknown compound. The computer print-out in figure 3 lists four of the compounds in order of their spectra's similarity to that of the unknown. Note that the similarity index (a quantitative assessment of spectra similarity) for 4-nitrobiphenyl is significantly higher than that of the compound whose spectrum was second-most like that of the unknown. In a similar manner the computer also correctly identified each of the three other carcinogens.

```
SPECTRUM NO. 320
RIVER WATER
  8 HITS
4-NITROBIPHENYL (SERL)^WNR DR^ 199 C12.H9.N.02 BSR 0518
FILE KEY= 9020
SIMILARITY INDEX= 0.854

5-BROMOACENAPHTHENE 232 C12.H9.BR API 1526
FILE KEY= 3872
SIMILARITY INDEX= 0.210

ANTHRAQUINONE (SEWL)^T C666 BU IUJ^ 208 C14.H8.02 BSR 0381
FILE KEY= 8865
SIMILARITY INDEX= 0.176

ACENAPHTHALENE 152 C12.H8 DOW 0925
FILE KEY= 2050
SIMILARITY INDEX= 0.157
```

Figure 3 : Computer Print-Out

When only compounds of known spectral characteristics are of interest, the dedicated computer can produce a limited mass reconstructed gas chromatogram (LMRGC), which contains responses from only those compounds containing pre-selected characteristic ion-fragments. Figure 4 shows an industrial effluent's LMRGC in which only compounds containing an ion fragment of mass-to-charge ratio 149 (typical of phthalates) were observed.

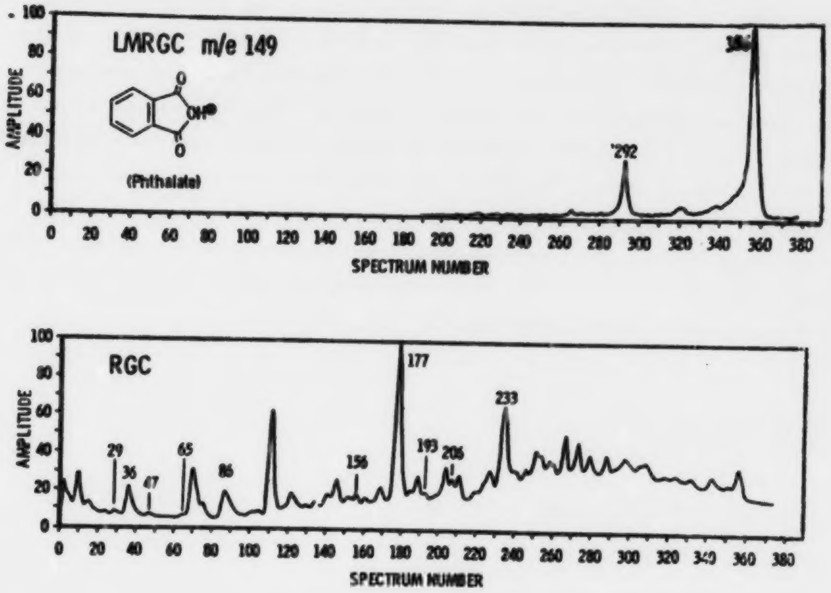

Figure 4 : Limited mass reconstructed gas chromatograph (LMRGC) only for ion fragments of mass-to-charge ratio 149 (typical of phthalates) and computer reconstructed mass gas chromatograph (RGC) of an industrial effluent.

In the conventional RGC (lower part of the photograph) GC peak 292 was obscured by other peaks. Techniques such as the LMRGC allow detection of compounds at concentrations as low as 0.01 µg/1.

International cooperative programs are now being developed for expanding the spectral library, which should result in a system that is indispensable in the assessment of environmental health effects.

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DISCUSSION

PERRY (U.K.)

1. You indicate that analysis is carried out on 1 liter of water containing 0.01 ug/liter of pollutants of which you only used a fraction. does this mean that mass spectrometric analysis can be carried out on 1 ng of material?

2. Can you define the spectral search routine and the meaning of "similarily index"?

DONALDSON (U.S.A.)

1. Yes. We have obtained satisfactory mass spectra when less than 1 nanogram of material was introduced to the gas chromatograph.

2. Briefly, the search routine takes advantage of the information redundancy of mass spectra and is based only on the two most intense peaks in every 14 atomic mass unit slot. There are four main steps:

1. Screening based on molecular weight range.
2. Screening based on most intense peak of the unknown spectrum
3. Pre-searching based on spectrum family.
4. Calculation of the similarity index and ordering of best matches based on peak-by-peak comparison of the unknown to those reference spectra that passed the pre-search.

The "similarity index" is a numerical index (ranging between zero and one) of the relationship between (1) the average ratio of corresponding peak intensities in the unknown and in the reference and (2) the fraction of unmatched peaks in both spectra. It simply describes how similar the spectrum in the computer file is to the spectrum of the unknown compound.

HARRISON (U.K.)

1. What procedure did you use for extraction of organic materials from water?

2. What was the efficiency of the extraction procedure and how did it vary with the concentration of solute in water and the level of suspended solids? Our own experience has shown that efficiencies under certain circumstances may be as low as 20%.

3. Which compounds are the carcinogens referred to? Were not the levels used in the synthetic samples unrealistically high and hence liable to give unreliable results for efficiency of extraction?

DONALDSON (U.S.A.)

1. The sample was extracted from the water, without pH adjustment, with methylene chloride in a separatory funnel.

2. It was not the intention of this paper to optimize extraction conditions for the four compounds selected for demonstration. We did not study extraction efficiencies since we were interested only in identification and not quantification. Our experience in extraction is similar to yours. A great deal needs to be done to improve extraction techniques.

3. The carcinogens were 4-aminobiphenyl, 4-nitrobiphenyl, N-(2-fluorenyl) acetamide and 3, 3-dichlorobenzidine, all selected from the OSHA list of carcinogens. Yes, the levels were unrealistically high. These compounds were selected to show that carcinogens could be identified by a computer from a group of 8,000 compounds, The technique, therefore, should be considered for application in studying health effects of drinking water. As stated in answer to your previous questions, no attempt was made to optimize extraction and concentration conditions, so the larger quantities were selected to allow identification even with poor extraction efficiencies. You are stressing a very important point: one can not identify compounds if he can't extract them. By no means would I recommend the extraction technique used here as optimum.

VERGLEICHENDE SCHWERMETALLANALYTIK MIT HILFE DER POLAROGRAPHIE UND ATOMABSORPTION - MÖGLICHKEITEN UND GRENZEN DER REPRODUZIERBARKEIT

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KURZFASSUNG

Für die Spurenanalyse von Schwermetallen wurden verschiedene Untersuchungsverfahren entwickelt, wobei sich u.a. inverspolarographische und atomabsorptionsflammenspektrometrische Methoden bewährt haben. Jedoch ist die Vergleichbarkeit der von verschiedenen Instituten erarbeiteten Untersuchungswerte häufig infrage gestellt, weil es noch an allgemein verbindlichen Standardvorschriften fehlt. Am beispiel der Bestimmung von Blei und Cadmium mit Hilfe der o. genannten Verfahren wird auf verschiedene instrumentelle Einflussfaktoren Bezug genommen, die nicht vernachlässigt werden dürfen, wenn die Reproduzierbarkeit gewährleistet werden soll. Hierbei sind folgende Grundsätze besonders zu beachten:

1. *Einhaltung optimaler Messbedingungen,*
2. *Erkennung und Beseitigung aller Störeffekte,*
3. *Kurvenkorrektion auf den Linearbereich,*
4. *Auswertung möglichst mit Hilfe von Eichkurvensystemen oder Einheitseichkurven.*

Bei Vorliegen dieser Voraussetzungen, die dem Analytiker zwar prinzipiell bekannt sind, aber einer einheitlicheren Handhabung bedürfen, kann die Reproduzierbarkeit merklich verbessert werden.

Es kommt daher in den Standardvorschriften nicht nur auf die alleinige Angabe des Messprinzipes an, sondern es müssen auch diejenigen Angaben in den Arbeitsvorschriften enthalten sein, die für die Einhaltung der durch das Messprinzip bedingten günstigen Messkonzeptionen wesentlich sind.

ABSTRACT

Various test methods for the analysis of heavy metals have been developed, of which inverse polarography and atomic absorption/flame spectrometry have been among the most effective. However, the comparability of experimental values obtained by various institutes is often questioned because there are still no generally binding standard regulations. Taking as an example the determination of amounts of lead and cadmium by means of the above-mentioned methods, reference is made to various instrumentation factors which must not be neglected if reproducibility is to be ensured. Particular attention must be paid to the following principles:

1. *Measurements must be made under optimum conditions,*
2. *All interference effects must be detected and eliminated,*
3. *Curve corrections must be made as regards the linear region,*
4. *If possible, calibration curve systems or unified calibration curves should be used to evaluate the results.*

If these conditions, with which the analyst is familiar in principle but which require a more uniform application, are satisfied, the reproducibility can be perceptibly improved. Thus what is important with regard to standard regulations is not only that the measuring method should be laid down, but that they must also contain the information required in order to maintain the conditions favourable to the application of the method.

1. Einleitung

Wenn man die historische Entwicklung der Untersuchungspraxis in der Spurenanalyse von Schwermetallen zurückverfolgt, so läßt sich feststellen, daß die herkömmlichen chemischen Verfahren (z.B. Gravimetrie, Titration u.ä.) vor etwa 15 Jahren durch physikalisch-chemische Methoden abgelöst und damit in mannigfacher und bedeutender Weise verbessert wurden. In Instituten mit routinemäßigem Untersuchungsbetrieb wie z.B. in der Landwirtschaftlichen Untersuchungs- und Forschungsanstalt (LUFA) Münster stiegen die Analysenzahlen hierdurch in diesem Zeitraum von wenigen Hundert auf jährlich ca. 100.000 an (Abb.1). Vielleicht aus verständlichen Gründen verfährt man gerade in Routinebetrieben allzu oft eingleisig, d.h. daß ein bestimmtes ausgewähltes Analysenverfahren und dieses möglichst im Serien- oder Massenbetrieb zur alleinigen Anwendung gelangt. Schon seit längeren Jahren streben wir aus verschiedenen Gründen zweigleisige Analysenmethoden an, u.a. auch, um durch Vergleiche die Möglichkeiten und Grenzen der Reproduzierbarkeit besser zu erkennen und um dem jeweils leistungsfähigeren Verfahren den Vorzug geben zu können. Auf diese Weise werden hier schon lange Inverspolarographie und Atomabsorptionsflammenspektrometrie nebeneinander betrieben. Als Untersuchungsmaterialien dienen Kulturpflanzen, Futtermittel, Böden und Stäube, sämtlich mit oder ohne Immissionsbelastung u.a. durch Blei und Cadmium.

2. Ausführungen zur Methodik

2.1 Inverspolarographie

Die Empfindlichkeit der inverspolarographischen Methode reicht auch unter Einhaltung optimaler Meßbedingungen im allgemeinen aus, um bereits die natürlich vorkommenden Gehalte an Blei und Cadmium in den genannten Untersuchungsmaterialien ermitteln zu können, im Gegensatz zur AAS in der Flamme, die diese Leistungsfähigkeit nicht oder nur bedingt besitzt. Bei der Inverspolarographie läßt sich mit wenigen Meßpunkten ein umfassendes Eichkurvensystem aufstellen -

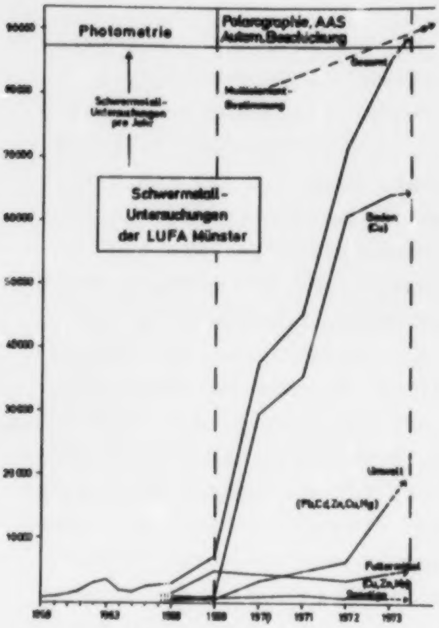


Abb. 1

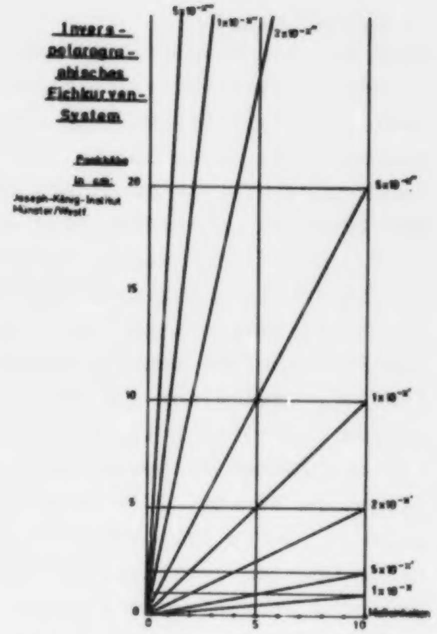
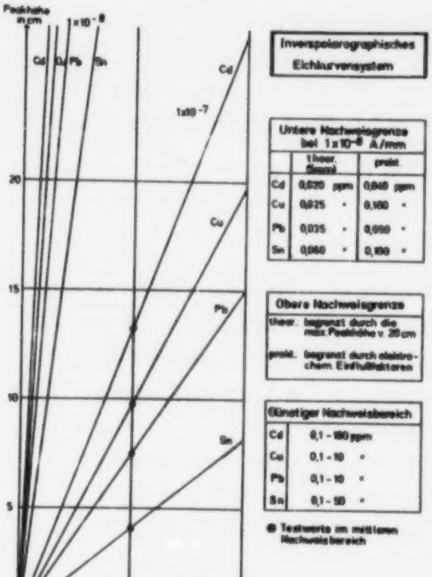


Abb. 2



Inverspolarographisches Eichkurvensystem

Untere Nachweisgrenze bei 1×10^{-8} A/mm	theor. (Sensi)	prakt.
Cd	0,020 ppm	0,040 ppm
Cu	0,025 "	0,100 "
Pb	0,035 "	0,050 "
Sn	0,060 "	0,100 "

Obere Nachweisgrenze

theor. begrenzt durch die max. Peakhöhe v. 20 cm

prakt. begrenzt durch elektrochem. Einflußfaktoren

Günstiger Nachweisbereich	
Cd	0,1 - 100 ppm
Cu	0,1 - 10 "
Pb	0,1 - 10 "
Sn	0,1 - 50 "

● Testwerte im mittleren Nachweisbereich

Abb. 3

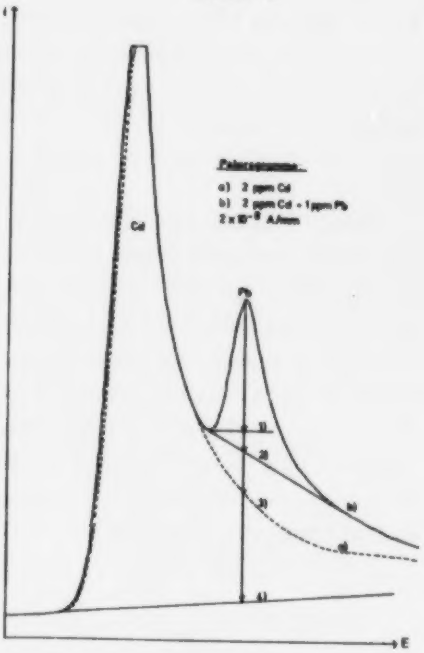


Abb. 4

Anlage: Tabelle 1

Methode bzw. Material	Nachweisbereiche / Ermittelte Gehalte
Blei (Pb)	0 (n.n.) 0.01 0.1 1 10 100 ppm
Inverspolarographie	mmmmmmmmmOOOOOOOOOOOOOOOmmmmmmmmm
AAS i.d. Flamme	mmmmmmmmmOOOOOOOOOOOOmmm
Weidelgras: ohne Immission n = ca. 100	Verlagerung des Meßbereichs durch Verdünnen leicht möglich ooooooooXooo
mit Immission n = >1300	ooooooooooooXoooooooooo
Futtermittel: n = 358	oooooooooooooooXoooooooo
Getreide n = 175	oooooooooooXooooooo
Sojaschrot n = 149	ooooooooXoooo
Fischmehl n = 34	oooooooXooooo
Industriestaub n = >2000	ooooooooooooooooooooooooooooooooooooooooooooooooooooooooXoo
Cadmium (Cd)	0 (n.n.) 0.01 0.1 1 10 100 ppm
Inverspolarographie	mmmmOOOOOOOOOOOOOOOOOOOOOOOOOOOOOmmm
AAS i.d. Flamme	mmmmmmmmOOOOOOOOOOOOOOOOOm
Weidelgras: ohne Immission n = ca. 100	oXo
mit Immission n = >1300	oooooooooooooXooooooooooo
Futtermittel: n = 358	ooooooooooooXooooooooooo Verschiebung des Meßbereichs durch Konzentrieren der Analysenlösung nur bedingt möglich
Getreide n = 175	ooooooooooooXoooooooo
Sojaschrot n = 149	ooooooooooooXoooo
Fischmehl n = 34	ooooooooooooooooooooXoooo
Industriestaub n = >2000	ooooooooooooooooooooooooooooooooXooooooooooooooooooooo
ooooooXoooooo Ø Gehaltsspanne	mmmmmOOOOOOOOOOOOmmmmmmmm min. Optimaler Meßbereich max. n.n. = nicht nachgewiesen

bestehend aus den Eichgeraden der verschiedenen Empfindlichkeitsstufen (1x10^{-6} bis 5x10^{-10} A/mm) -, das für jedes Element individuell verschieden ist und im übrigen den Vorzug hat, daß man die Konzentration *einer* Lösung an verschiedenen Punkten dieses Eichkurvensystems messen kann (Abb. 2 u. 3). Dies ist eine wesentliche Auswertungshilfe, da die jeweils korrespondierenden Punkte des Eichkurvensystems in einem bestimmten Korrelationsverhältnis zueinander stehen. Dadurch können auch die nach einem Testwert zu erwartenden Peakhöhen namentlich im Hinblick auf die optimalen Meßbedingungen vorausberechnet und im übrigen ferner etwaige auftretende Störeffekte frühzeitiger erkannt werden.

Es ist aber zu berücksichtigen, daß die Elemente mit niedrigerem Halbstufenpotential die Grundlinien der nachfolgenden Elemente und dadurch auch ihre konzentrationsbedingten Peaks verschieben. Zwar kann man diese sich ergebenden Peakerhöhungen genau berechnen, da sie von der jeweiligen Konzentration der Elemente und ihrer Halbstufenpotentialdifferenz abhängig sind. Bei der Durchführung von Routineanalysen ist das jedoch ein erschwerendes Moment, weil die in der Auswertung üblichen Hilfslinien (z.B. 1) die Abklingkurve oder 2) die Horizontale oder 3) die Minimumtangente) leicht zu Fehlberechnungen führen können (Abb. 4). Um die Inverspolarographie reproduzierbar anzuwenden, muß der Schreiber unmittelbar nach Erreichen jeder Peakspitze durch kurzzeitiges Abschalten des Spannungsvorschubs auf die Grundlinie zurückgeführt werden (Abb. 5). Auf diese Weise kann man bei jedem Element mit verschiedenen, d.h. den jeweils günstigsten Empfindlichkeitsstufen messen, und die Auswertung der Peaks läßt sich außerdem nach vorberechneten allgemeingültigen Tabellenwerten vornehmen. Zwischen den Zahlenreihen kann interpoliert werden.

Systemabweichende Zahlenwerte bei Peakvermessungen weisen auf Störeffekte hin. Evtl. durch Eisen hervorgerufene Peakverzerrungen oder -depressionen sollten besser mit Ascorbinsäurezusatz als durch Methylisobutylketon beseitigt werden, weil dadurch ein Arbeitsgang zu ersparen ist und zusätzliche Fehlermöglichkeiten ausscheiden.

2.2 Atomabsorption i.d. Flamme

Diese Methode ist aufgrund der leichteren Bedienungsweise und der Möglichkeit der automatischen Beschickung des Gerätes mit Probenlösungen beliebter und erlaubt eine größere Meßfrequenz pro Zeiteinheit. Auch ist der Anwendungsbereich evtl. bei Skalenspreizung, Brennerverstellung und Benutzung verschiedener Wellenlängen sehr breit, jedoch für die Gehaltslagen von Pflanzenmaterial ohne größere Immissionsbelastung meist nicht empfindlich genug, so daß ihr Einsatz, wenn man das Prinzip der optimalen Meßbedingungen befolgen möchte, häufiger fraglich bleibt. Unter diesen Gegebenheiten kann nur dann eine günstige Reproduzierbarkeit erwartet werden, wenn auch hier die vom Meßinstrument ausgehenden Einflußfaktoren nicht willkürlich zur Geltung gelangen. Die Fehlermöglichkeiten sind besonders groß im nichtlinearen Teil der Eichkurven, der damit wenigstens für die Routineanalyse kein Bereich der optimalen Meßbedingungen ist. Für den nichtlinearen Bereich liefern die Hersteller von Flammenphotometern als Zubehör u.a. Kurvenkorrektoren, wobei Eichpunkte mit einer Abweichung bis zu 30 % auf den Linearbereich projiziert werden. Messungen mit Cadmium (Cd) haben aber z.B. ergeben, daß bei Auftragung von Absorption gegen beliebige Konzentrationsverhältnisse (C_n/C_{max}) stets gleiche Kurven erhalten werden, die ungefähr erst beim Konzentrationsverhältnis 0,5 von der Geraden abweichen (Abb. 6 u. 7). Dadurch ist es möglich, auch ohne Kurvenkorrektor im linearen Bereich zu arbeiten, wenn das Gerät mit der doppelten maximal zu messenden Konzentration auf die Absorption 1,0 eingestellt wird. In Anbetracht des großen Meßbereiches der AAS - namentlich bei Brennerverstellung - ist die Einengung des jeweiligen Meßbereiches um den Faktor 2 im Sinne einer ver-

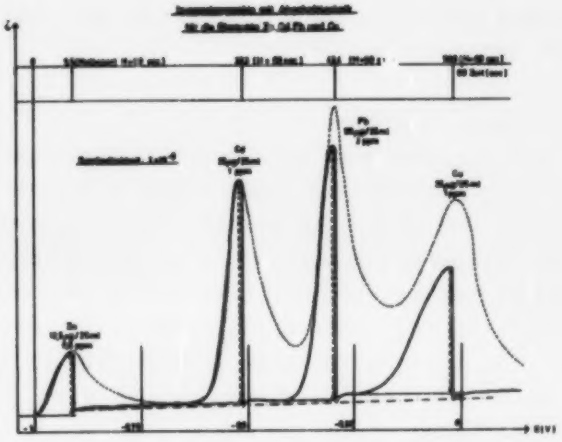
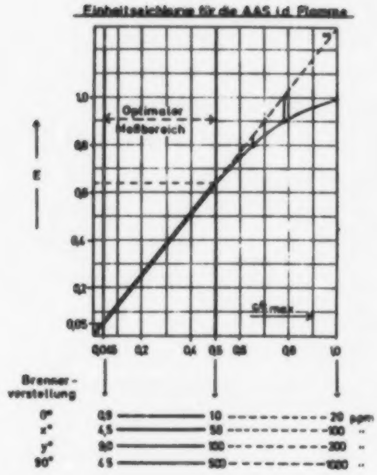


Abb. 5



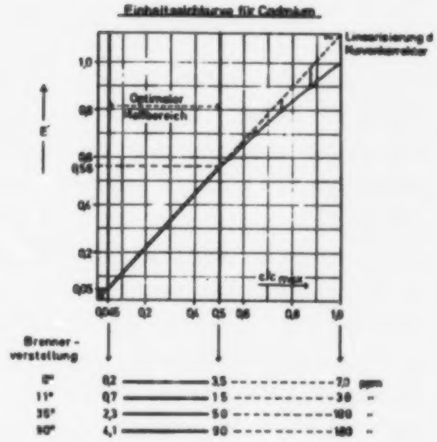


Abb. 6 : * Verlängerung des Meßbereiches durch Skalenspreizung bis zur Nachweisgrenze

** Linearisierung außerhalb des optimalen Meßbereiches durch Kurvenkorrektor

Abb. 7 : * Verlängerung des Meßbereic durch Skalenspreizung bis 0,01 ppm

Wellenlänge: 228,8 nm
Lampenstrom: 3 m Amp

besserten Reproduzierbarkeit durchaus hinzunehmen. Für den Routinebetrieb genügt die Aufstellung einer Einheitseichkurve mit entsprechender Aufteilung des gesamten Nachweisbereiches. Im Falle der Brennerdrehung (Lichtwegverkürzung) ist hier - bei sonst gleichen Versuchsbedingungen - eine Angabe über die (leicht meßbare) Winkelverstellung erforderlich. Dieses Prinzip ist auch bei der Bestimmung anderer Elemente zu empfehlen, so daß hier ebenfalls ein Eichkurvensystem aufgestellt werden kann. Die Verhältnisse liegen günstiger als beim Cadmium, wenn mehr als die Hälfte der Eichkurve linear verläuft, und ungünstiger, wenn die Absorptionskurve schon weiter unterhalb 0,5 vom linearen Verlauf abweicht wie z.B. beim Zink ca. 0,4 oder bei Blei und Kupfer je ca. 0,3.

3. Schlußfolgerungen

Vergleicht man Brauchbarkeit und Einsatzfähigkeit der beiden Untersuchungsverfahren (Inverspolarographie und AAS i.d. Flamme) für die Spurenanalyse von Schwermetallen am Beispiel von Blei und Cadmium, so kommt man zu dem Ergebnis, daß zwar beide Methoden für die Anwendung in der Umweltanalytik grundsätzlich geeignet sind, jedoch mit der Einschränkung, daß ihre wechselseitige Benutzung zu empfehlen ist. Infolge der unterschiedlichen Meßprinzipien und der dadurch bedingten eigenen instrumentellen Abhängigkeitsfaktoren decken sich die optimalen Meßbereiche nur teilweise, so daß nicht selten sogar ausschließlich eine der beiden Methoden zur Wahl steht (vgl. Tabelle 1). Der optimale Nachweisbereich gewährleistet aber allein nicht das Maß der Reproduzierbarkeit, da hierfür ferner von entscheidender Bedeutung ist, daß (mehr) Vereinheitlichung im technischen Vorgehen bei der Erzeugung und Auswertung der Meßdaten erreicht wird. Zur Verbesserung der Reproduzierbarkeit gehören entsprechende Angaben - auf die im Text hingewiesen wurde - in die Untersuchungsvorschriften namentlich, wenn diese rechtsverbindlichen Charakter haben sollen.

DISKUSSION

VALENTA (Bundesrepublik Deutschland)

I) Wir haben festgestellt, dass bei der Messung des Bleigehalts im Blut mit der Inverspolarographie die Methode der Standardzugabe vorzuziehen ist, weil dabei der Einfluss der organischen Matrix eliminert werden kann. Haben Sie bei Ihren Messungen einen solchen Einfluss der Matrix nicht festgestellt?

2) Die Messung der Peakhöhe von der Nullinie des Stromes ist sicher am genauesten. Die Voraussetzung dafür ist aber, dass der Reststrom bei verschiedenen Proben immer derselbe ist. Haben Sie das überprüft?

3) Die Beeinflussung der benachbarten Peaks, wie von Blei und Kadmium, kann man weitgehend durch Anwendung der Differentialpulspolarographie beseitigen.

RETHFELD (Bundesrepublik Deutschland)

I) Wir untersuchen hauptsächlich Pflanzenmaterial. Die Abschaltemethode (d.h. Abschalten des Spannungsverschubs nach Erreichen der Peakhöhe, der Stromkreis wird nicht unterbrochen) haben wir zunächst an Standardlösungen ausprobiert. Die Schwermetallgehalte in Pflanzen sind sehr hoch im Vergleich zu tierischen Organen. Dadurch ist die Störung nicht so ausschlaggebend.

2) Bei uns handelt es sich meistens um grosse Serien ein- und derselben Substanz. Der Reststrom bleibt dann annähernd konstant.

3) Die Abschaltung des Spannungsvorschubes wird bei uns noch von Hand vorgenommen. In der Landesanstalt für Bodennutzungs- und Immissionsschutz, Essen, ist die Abschaltung automatisiert. Die Differentialpulspolarographie steht uns nicht zur Verfügung.

SPURENNACHWEIS SCHÄDLICHER ELEMENTE IN LUFT, WASSER UND BIOLOGISCHEN MEDIEN MIT DER RÖNTGENFLUORESZENZANALYSE

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KURZFASSUNG

Zur Untersuchung der Wirkung der Umweltverschmutzung auf den Menschen ist die chemische Überwachung der Bereiche - Luft-Wasser-Boden - sowie die Kontrolle pflanzlicher und tierischer Produkte von grundlegender Bedeutung.

Neuere Untersuchungen haben ergeben, dass die Röntgenfluoreszenzanalyse - als zerstörungsfreies Analysenverfahren - erfolgreich zur Lösung der oben angesprochenen Probleme eingesetzt werden kann.

Zur chemischen Überwachung der Luft werden Spurenelemente, die an Aerosole gebunden sind, auf geeignete Filterpapiere angereichert. Ein Vergleich mit Standardproben gestattet eine quantitative Analyse mit 1 bis 10% relativer Genauigkeit. Die Nachweisgrenzen liegen - je nach Element - bei 1 bis 30 ng/cm^2 Filterfläche.

Bei der Wasseranalyse werden über Anreicherungsverfahren - je nach Element und Anreicherung - Nachweisgrenzen von 0,1 µg/l bis 50 µg/l erreicht.

Die Analyse von Schadmetallen im Pflanzenmaterial erfolgt an getrocknetem, zerkleinertem und tablettiertem Material. Die

erreichbaren Nachweisgrenzen liegen bei 0,1 bis 0,5 ppm. Bei Veraschung des Materials wird diese Grenze um den Faktor 6 reduziert.

Untersuchungen an getrockneten, pulverisierten und tablettierten Fleischproben ergaben für Pb, As, Hg und Cd Nachweisgrenzen von 20 bis 30 ppb (0,02 bis 0,03 ppm).

ABSTRACT

For the investigation of the effect of environmental pollution on man, chemical monitoring of air, water and earth and also checks on vegetable and animal products are of fundamental importance.

Recent research has shown that X-ray fluorescent analysis, being a non-destructive analytical method, can be used successfully to solve the above-mentioned problems.

For chemical monitoring of the air, trace elements combined with aerosols are concentrated on suitable filter papers. A comparison with standard samples permits quantitative analysis within a relative accuracy of 1 to 5%. The detection limits are within the range of 1 to 30 ng/cm^2 filter surface, depending on the element.

In water analysis, concentration processes enable detection limits of 0.1 μg/l to 50 μg/l to be achieved, depending on the element and the concentration.

The analysis of noxious metals in vegetable matter is car-

ried out on dried, crushed and pelletized substances. The detection limits attainable are between 0.1 and 0.5 ppm. If the substance is incinerated, this limit is reduced by a factor of 6.

In tests on dried, crushed and pelletized meat samples the detection limits were 20 to 30 ppb (0.02 to 0.03 ppm) for Pb, As, Hg and Cd.

1. Einleitung

Zur Untersuchung der Wirkung der Umweltbelastung auf den Menschen ist die chemische Überwachung der Bereiche-Luft-Wasser-Boden- sowie eine laufende Kontrolle pflanzlicher und tierischer Produkte von grundlegender Bedeutung. Neuere Untersuchungen haben ergeben, dass die Röntgenfluoressenzanalyse (RFA) als zerstörungsfrei arbeitendes Analysenverfahren erfolgreich zur Lösung der oben angesprochenen Probleme eingesetzt werden kann.

Wesentliche Vorteile der RFA sind eine kurze Analysenzeit, eine vollständige Automatisierbarkeit sowie die Möglichkeit der Archivierung des untersuchten Probengutes.

2. Die Analyse schädlicher Elemente in der Atmosphäre

Zur Analyse der Luft werden Spurenelemente, die an Aerosole gebunden sind, auf geeignete Filter [1] angereichert, indem definierte Luftvolumina durch diese Filter gesaugt werden. Derart mit Staub belegte Filter können ohne Nachbehandlung im Spektrometer gemessen werden [2] .

Die Eichung des Verfahrens erfolgt mit Standardproben, die wie folgt präpariert werden: Auf die in der Praxis zur Staubabscheidung verwendeten Filterpapiere (Whatman oder Millipore) werden 50 bis 100 µl Eichlösung gegeben. Die Messung der Standardproben unter optimalen Bedingungen ergibt lineare Eichkurven.

Nach der Eichung ist es notwendig, Korrekturfaktoren für die zu analysierenden Elemente zu finden, welche die unterschiedliche Absorption der gemessenen Röntgenstrahlung an den mit Eichlösungen und den mit Stäuben belegten Filtern berücksichtigt. Die Bestimmung dieser Korrekturfaktoren K erfolgt über eine gesicherte chemische Analyse des mit Staub belegten Filters. Die mit der RFA erhaltenen Analysenwerte C ergeben sich dann zu:

$$C_{Staubfilter} = C_{Eichung} \times K \text{ in } \mu g/cm^2 \text{ Filterfläche}$$

3. Die Wasseranalyse

Die oben beschriebene Filtermethode kann auch zur Analyse des Wassers eingesetzt werden. In diesem Fall werden 100 µl Wasser auf die Filterpapiere gegeben. Die Tabelle 1 zeigt die mit dieser Methode erreichbaren Nachweisgrenzen für Aerosole und Wasser.

Die Nachweisgrenzen lassen sich durch Anreicherungsverfahren reduzieren: Durch Eindampfen einiger Liter Wasser und Tablettieren des Rückstandes erhält man die in Tabelle 2 angegebenen nachweisbaren Grenzkonzentrationen. Eine weitere Anreicherung der Schadstoffe erhält man durch chemische Abtrennung der Hauptkomponenten (Ca- und Mg-Verbindungen) und Vermessen des Niederschlages (Tabelle 2).

4. Die Schadmetallbestimmung in pflanzlichen Produkten

Die Analyse von Schadstoffen in Pflanzenmaterial erfolgt an getrocknetem, zerkleinertem und tablettiertem Material.

Zur Herstellung von Eichproben werden einem chemisch analysierten Ausgangsmaterial Eichlösungen zugegeben, welche die zu analysierenden Elemente in abgestuften Konzentrationen enthalten. Das so entstandene Suspensat wird homogenisiert und getrocknet. Das getrocknete Material wird bei Zugabe eines organischen Bindemittels erneut homogenisiert und zu Tabletten verpresst..

Bild 1 zeigt die aus Eichkurven Standardabweichungen S_x für die Elemente Pb, As, Hg, Se, Zn und Mn als Mass für die Analysengenauigkeit mit

$$S_x = \frac{\sqrt{Nx}}{m\ Cx} \times 100\% \text{ relativ}$$

Tabelle 1: Mit der RFA erreichbare Nachweisgrenzen Cg schädlicher Elemente an Aerosolen und im Wasser mit Filtermethode

Cg	Na	Mg	Al	Si	S	Cl	K	Ca	V	Fe	Zn	As	Cd	Pb
Cg (Lösung) (ng/cm^2)	57o	79	1o,4	6,1	7,1	22	1,2	1,4	7,4	12,8	17	94	4,7	3o
C_L(ng/m^3)	23oo	32o	44	25	29	9o	4,9	5,7	3o	52	69	38o	19	12o
C_W (ppm)	52	7,2	o,94	o,55	o,64	2,o	o,11	o,13	o,67	1,2	1,6	8,5	o,43	2,7

C_L bezogen auf 1 m^3 Luft (ohne Korrektur K)

C_W bezogen auf loo/ul Wasser

Tabelle 2 **Nachweisgrenzen in Wasser nach Anreicherung**

Element	Messzeit sec	Nachweisgrenze /ug/l	
		Eindampfen	Abtrennen (H_2S-Niederschlag)
Na	1oo	1o	
Mg	1oo	5	
S, K, Ca, Cu, Fe	4o	ca 1	
Fe, Ju, Zn, Co, Pb, As, Mo, W	4o	o,1 ... o,5	o,o1 ... o,o5

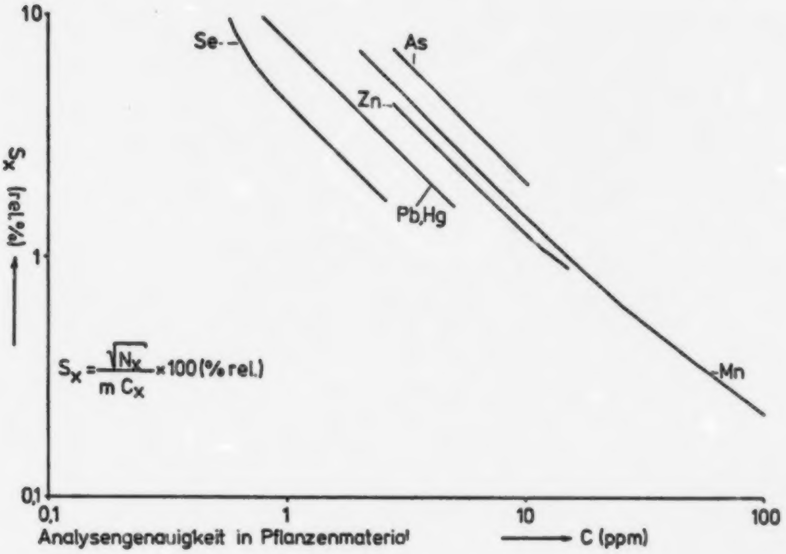


Bild 1

Nx = die in der Zeit T an der Konzentration C_x gemessene Impulszahl

m = Steigung der Eichkurve

Nach Bild 1 beträgt die Standardabweichung im Bereich 1 bis lo ppm lo bis 1% relativ.

Die Eichkurven sind auch hier - wie allgemein in der Spurenanalyse - linear.

In der Tabelle 3 sind die mit dieser einfachen Präparation in einer Messzeit T = 2oo sec erreichbaren Grenzkonzentrationen eingetragen.

Zur Herabsetzung der Nachweisgrenze bis in den ppb-Bereich müssen Anreicherungsmethoden wie Veraschung oder Extraktion herangezogen werden.

Tabelle 3 **Nachweisgrenzen und Analysengenauigkeiten an getrocknetem Pflanzenmaterial**

Element	Meßzeit (sec)	Analysengenauigkeit *) (ppm)	Nachweisgrenze *) ppm
Mn	200	10 ± 0,3	0,4
Cu	200	10 ± 0,3	0,4
Zn	200	8 ± 0,24	0,36
Se	200	1 ± 0,15	0,13
Pb	200	2 ± 0,08	0,2
As	200	6 ± 0,18	0,5

*) für S = 99,7 %

Eine Pb-Bestimmung an getrocknetem und veraschtem Material ergab an getrocknetem Material eine Nachweisgrenze Cg von o,2 ppm, an veraschtem Material ein Cg von o,o33 ppm in T = 2oo sec. Durch Verlängerung der Messzeit kann Cg wie folgt verbessert werden:

$$Cg_2 = Cg_1 \sqrt{\frac{T_1}{T_2}}$$

Cg_1 = Nachweisgrenze bei einer Messzeit T_1

Cg_2 = Nachweisgrenze in der Messzeit T_2

5. Die Analyse tierischer Produkte

Von hochaktuellem Interesse ist die Schadmetallbestimmung an tierischen Produkten:
Hier hat sich folgende Präparation bewährt:
Ca 2o g des Produktes, z.B. eine Fleischprobe, werden grob zerkleinert, mit 2o ml Wasser versetzt und homogenisiert. Das Homogenisat wird durch Vakuum- oder Gefriertrocknung entwässert. Das getrocknete Material wird pulverisiert und kann mit oder ohne Bindemittel zu Tabletten verpresst werden. Diese Tabletten können direkt im Spektrometer vermessen werden.

Zur Herstellung von Standardproben werden dem chemisch analysierten Material nach der Grobzerkleinerung 2o ml Schwermetallsalzlösungen in abgestuften Konzentrationen zugegeben.

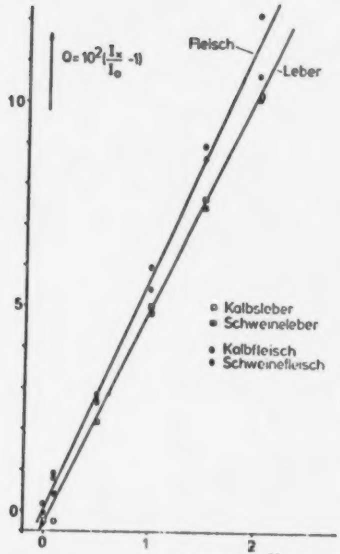
Die weitere Präparation erfolgt wie eingangs beschrieben. Zur Eliminierung von Matrixeinflüssen [4] bei wechselnder Fleischmatrix kann die Eichung mit einem N_o-Wert ("background") als innerer Standard durchgeführt werden.

Tabelle 4 **Nachweisgrenzen für Schadmetalle in Fleisch**

Element	Linie	T = 200 s	T = 400 s	T = 1 000 s
Pb	$L\alpha$	0,07	0,049	0,03
Pb	$L\beta_{1,2}$	0,075	0,053	0,03
As	$K\alpha$	0,035	0,025	0,015
Hg	$L\alpha$	0,065	0,046	0,03
Sb	$L\beta_1$	0,55	0,39	0,25
Cd	$K\alpha$	0,076	0,054	0,03

$Cg = \frac{3\sqrt{N_o}}{m}$; N_o Untergrundimpulszahl

m Steigung der Eichkurve



Hg-Eichung mit I_o als innerem Standard

Bild 2

Bild 2 zeigt eine derart ermittelte Eichkurve zur Hg-Bestimmung an Fleisch und Leber. Aus Bild 2 geht hervor, dass sowohl Kalb- als auch Schweinefleisch - die sich in ihrem Fettgehalt wesentlich unterscheiden - mit einer Eichkurve erfasst werden können. Das gleiche gilt für Kalbs- und Schweineleber.

Tabelle 4 gibt schliesslich die Nachweisgrenzen für Pb, As, Hg, Sb und Cd wieder, die mit der einfachen Präparation der Trocknung in 2oo, 4oo und 1 ooo sec. Messzeit erhalten wurden.

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DISKUSSION

DAMS (Belgien)

Ich habe eine Frage bezüglich des Berichtigungsfaktors, der bei der Analyse von auf Filtern gesammelten Aerosolen erforderlich ist. Dieser Berichtigungsfaktor kann bei leichten Elementen wie Na, Mg, Al usw. sehr hoch, bis zu IO sein. Der Faktor ist abhängig vom Filtertyp, von der Eindringungstiefe in den Filter und von der Absorption des Staubes selbst. Die Eindringungstiefe der Aerosole in den Filter hängt wiederum ab von der Luftgeschwindigkeit und dem Filtertyp, aber auch von der Partikelgrösse und der Verteilung von Masse/Grösse des Elements als Funktion der chemischen Zusammensetzung. Meines Erachtens würde ein "Treib-"(puff) Verfahren zur Ausarbeitung der Normen einen Teil der Probleme lösen, wenn eine Aerosol-Standardprobe homogen auf einem Filter verteilt wird. Waren Sie in der Lage, konstante Berichtigungsfaktoren zu ermitteln?

BEITZ (Bundesrepublik Deutschland)

Die Grösse der Korrekturfaktoren bei der Analyse von auf Filtern gesammelten Aerosolen ist abhängig vom analysierten Element, vom Filtertyp und vom Staubsammelgerät.

Bei Konstanthaltung des Filtertypes, des Staubsammelgerätes und der Staubsammelbedingungen (Druck, Geschwindigkeit usw.) ist der Korrekturfaktor abhängig von der Absorption des Staubes.

Für Schwefel fanden Bonnevie-Svendson und Follo vom Institut für Atomenergie in Kjellar Norwegen, einen Korrekturfaktor K = 0,66.

Zu gleichen Ergebnissen kamen G. Rönnicke, Aerosolmessstelle Schauinsland, 78OI Schallstadt-Wolfenweiler, BRD und D. Klockow, Institut für anorganische Chemie, Freiburg/Brg. BRD,

Rönnicke und Klockow haben in jüngster Zeit auch Korrekturfaktoren für weitere Elemente bestimmt. Zahlenwerte sind z.Zt. noch nicht veröffentlicht.

1431

UNTERSUCHUNG DER WIRKUNGEN AUF DEN MENSCHEN
EXPOSURE MONITORING
MESURE DE L'EXPOSITION
MISURA DELL'ESPOSIZIONE
METING VAN EXPOSIE

Vorsitzender - Chairman - Président - Presidente - Voorzitter

G.C. BUTLER (Canada)

ETUDE PREPARATOIRE EN VUE DE L'ETABLISSEMENT D'UN PROGRAMME COORDONNE DE SURVEILLANCE DE LA CONTAMINATION DE L'HOMME PAR LES PRODUITS CHIMIQUES

E. FOURNIER

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RESUME

Le projet H.M.P. s'efforce d'étudier les intoxications subchroniques et chroniques liées à l'environnement chimique moderne, les intoxications aiguës étant étudiées par ailleurs.

Le projet doit porter sur des observations de très longue durée à forte dispersion écologique, donc difficiles et coûteuses. C'est cependant le seul moyen de définir des paramètres de surveillance et de valider des observations cliniques réparties au hasard.

Le projet comprend la surveillance régulière d'échantillons de population représentatifs d'un ensemble suffisant, la surveillance spécifique de certaines populations particulièrement exposées ou particulièrement sensibles: étude professionnelle, pharmacovigilance, groupes humains sentinelles en particulier allergiques.

Une banque de données toxicologiques par collecte aléatoire est une organisation indispensable à la recherche des coïncidences suspectes. Elle participe à la coordination d'un projet qui tend à répondre aux inquiétudes manifestées devant le "danger chimique" par l'ensemble des populations à civilisation industrialisée.

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ABSTRACT

The HMP is aimed at studying chronic and sub-chronic poisoning caused by the chemicals in the modern environment, acute poisoning being dealt with in another study.

The project must be based on observations over a very long period and with a wide ecological distribution, and so they will be difficult and expensive. This is, however, the only way of defining surveillance parameters and of validating random clinical observations.

The project involves the regular surveillance of population samples representative of an adequate total population, as well as specific surveillance of certain groups which are particularly exposed or particularly sensitive: professional studies, pharmacological control, pilot groups of people - particularly those with allergies.

A bank of toxicological data obtained by random sampling is indispensable for research into suspicious coincidences. This data bank will help to coordinate a project which reflects the disquiet about the "chemical danger" felt by all people in industrialised countries.

1/ L'établissement d'un programme coordonné de surveillance de la contamination de l'homme par les polluants chimiques constitue la base d'une information scientifique en vue de l'évaluation objective des risques que fait peser la pollution sur la santé publique.

1 - 1/ Le projet H.M.P. doit éviter la confusion des secteurs ou phases de la toxicologie clinique :

Phase 1 : Intoxications aiguës : Accidents, suicides, crimes.

Phase 2 : Intoxications subaiguës et chroniques : Maladies professionnelles Maladies médicamenteuses. Tératogénèse. Allergie.

Phase 3 : Intoxications chroniques : Cancérogénèse. Mutagénèse. Vieillissement. Fluctuations allergologiques et immunologiques. Imprégnations toxiques.

A ces phases correspondent des organisations particulières :

Phase 1 : Les Centres Anti-Poison ont déjà répondu à la première demande.

Phase 2 : Les Centres de Médecine du Travail, les Centres Anti-Poison, les Centres de Pharmacovigilance peuvent s'organiser pour répondre ensemble à la deuxième demande.

Phase 3 : Chacun des centres de la Phase 2 peut participer à un travail d'ensemble.

1 - 2/ Difficultés particulières de réalisation :

La troisième phase, spécifique du projet H.M.P., ne devrait être explorée que progressivement et avec beaucoup de prudence pour trois raisons essentielles :

- la très longue durée nécessaire à l'observation réellement chronique, oblige à tenir compte d'une foule d'interférences dont l'effet propre peut être supérieur à ceux que l'on pourrait attribuer à l'environnement. Commencer la phase 3 sans assurer la sécurité scientifique de la phase 2, exposerait à des erreurs très grossières.
- la forte dispersion écologique des conditions de vie et l'interférence avec des habitudes déviantes jouent un rôle essentiel en pathologie chronique : nutrition anormale, alcoolisme, tabagisme, absorption régulière de médicaments.
- la rareté des opérations régulièrement conduites dans cet esprit de recherche est due à la difficulté et au coût d'opérations portant sur des centaines de références acquises sur chacun des individus étudiés grâce à la définition des paramètres biologiques.

1 - 3/ Aspects psycho-sociologiques

Il serait inutile de prévoir d'aussi importants projets et de les doter d'une validité scientifique sans prendre en considération en même temps les conséquences psycho-sociologiques de telles entreprises. Les conséquences d'une étude toxicologique font toujours apparaître une certaine forme de responsabilité judiciaire, une certaine possibilité de contrôle technologique et de modification de l'utilisation, des exigences nouvelles de contrôle et de prévention ; elles suscitent beaucoup de discussions.

2/ Tout projet H.M.P. doit suivre un plan rigoureux et comprendre :

- une recherche programmée spécifique du projet H.M.P. et d'une substance chimique précise ;
- une action de coordination des centres de Phase 2 sans modifier leur activité spécifique ;
- l'adjonction à chaque groupe coordonné d'une activité H.M.P.

Après une période de fonctionnement, de nouvelles améliorations peuvent être proposées.

2/1La recherche exhaustive des maladies nouvelles effectivement liées à une contamination chimique est l'un des objectifs du projet H.M.P. Il ne peut être réalisé. D'où l'idée d'une Banque des appels et des demandes d'informations à propos de coïncidences suspectes ou de maladies inexpliquées ... (Banque de collecte quasi-aléatoire - B.C.A.). L'accumulation des données aléatoires peut faire apparaître des coïncidences assez régulières pour devenir démonstratrices d'un phénomène multifactoriel de toxicité distribuée au hasard (spérergique) et nous pensons que c'est le seul moyen à mettre en oeuvre actuellement par H.M.P., en débutant l'opération initiale par la phase 2 (enregistrement aussi organisé que possible des affections des ouvriers "anormalement" exposés, des êtres humains particulièrement sensibles (sujets sentinelles), des réactions adverses aux médicaments, aux pesticides, aux produits de maison). L'identité des troubles cliniques a permis le diagnostic de toutes les intoxications chroniques collectives récentes, ce qui justifie l'espoir d'un résultat dans cette direction de recherches.

2/2Surveillance régulière d'échantillons de population

La surveillance régulière d'un échantillon de population est une autre voie d'abord de H.M.P. (Phase 3). Ses buts doivent être précisés, ce qui suppose :

a) la définition de la population
b) la définition de l'échantillon

c) la description des limites du projet

d) la recherche des résultats prévisibles

La définition des groupes témoins dans chaque pays permettrait :

- de fournir des renseignements acceptables pour décider de la surveillance de la population et de la rédaction de mesures préventives.
- de fournir un document de base sur la contamination réelle de chaque population permettant dans une certaine mesure de comparer les types alimentaires, les types de contaminations chimiques de base liées à l'écologie, au type de civilisation, leurs effets sur le fréquence de certaines maladies très courantes.
- d'aboutir par le moyen indirect de la surveillance systématisée, répertoriée tous les trois ans, à une étude extensive portant sur environ 10 000 sujets, groupe global important mais à peine suffisant pour apprécier l'apparition de maladies rares ou comparer la fréquence de maladies communes.
- ce projet se situerait par rapport aux méthodes courantes de surveillance comme un axe de référence sans pour autant éliminer les autres voies d'observation et les autres études qui devraient s'y référer dans la mesure où leur impact statistique se rapprocherait de la surveillance de un pour 25 000 habitants, en poursuivant des buts parallèles.
- Il faudrait en outre isoler des groupes humains "anormalement" exposés (phase 2), ou anormalement réceptifs. Leur étude doit être organisée dès que possible au titre de la phase 2. Les sujets "anormaux" : les ouvriers spécialement exposés, les organismes sentinelles par anomalie congénitale ou acquise, doivent être rapportés au groupe où ils se trouvent, celui-ci faisant souvent l'objet d'une surveillance médicale particulière.

3 / Réalisation du programme

Toute opération H.M.P. devrait ensuite se faire en trois temps, après le choix des sujets, des paramètres biologiques utiles et comparables, et de l'échantillon de la population à étudier :

3/1 préparation et collecte des documents :

Aucun document acceptable ne peut être recueilli par des personnes incompétentes. D'où l'idée formelle d'éliminer du temps de préparation et de collecte des documents toxicologiques toute organisation non habilitée par une compétence technique, c'est-à-dire par une expérience suffisante confrontée à celles d'autres laboratoires analogues.

3/2 étude critique des résultats bruts : observation et dosages.

3/3 validation des résultats retenus et corrélations avec d'autres opérations portant sur le même sujet. Formation des Laboratoires.

- d'abord définir les laboratoires et groupes cliniques compétents ou faciliter l'accès à la compétence de ceux qui souhaitent participer au programme H.M.P.
- puis proposer les sujets à traiter en commun et définir les collaborateurs possibles, les paramètres retenus, les méthodes acceptées, le type de collecte organisée.

Les laboratoires de Toxicologie subaiguë (phase 2), assez nombreux, sont proches des services de Médecine du Travail, zone élective de collecte de ce type de désordres, des Services Hospitaliers pour ce qui concerne les accidents thérapeutiques ou l'allergie aux substances chimiques. Des laboratoires spécialisés existent dans les grands centres de médecine d'entreprise, dans certains départements hospitalo-universitaires : Centres anti-poison, Service de Pathologie Industrielle, Services de Pharmacovigilance.

L'activité de l'ensemble se complète normalement par des études socio-psychiatriques touchant les toxicomanes, l'ergonomie, les déviants alimentaires, et par des études épidémiologiques visant à démontrer le danger de nouveaux produits manipulés par grandes quantités.

Les laboratoires de Toxicologie chronique (phase 3), essentiellement celle de l'environnement, seraient typiques d'une activité épidémiologique greffée sur des études cliniques et expérimentales, mais ils sont exceptionnellement orientés vers des études de toxicologie humaine.

Assez paradoxalement, les laboratoires de toxicologie des grands instituts médico-légaux peuvent jouer un rôle essentiel dans ce domaine en permettant, grâce au grand nombre d'autopsies de sujets accidentés probablement sains, de fournir des échantillons représentatifs de la population régionale normale ou tout au moins contrôlable, et d'effectuer les mesures nécessaires.

La collecte peut aussi se faire dans les centres de pathologie (ou d'anatomo-pathologie) des hôpitaux universitaires importants. Selon les cas, le laboratoire de toxicologie médico-légale ou le laboratoire de chimie médicale hospitalier ou universitaire, assurera les dosages.

Le bénéfice réel à tirer d'un projet H.M.P. sera en fait une modification de l'esprit des études toxicologiques en favorisant les discussions entre personnes compétentes dans les domaines différents et en permettant d'exposer l'ensemble des problèmes aux responsables gouvernementaux.

DISCUSSION

WASSERMANN (Israel)

Les modèles que l'auteur suggère pour l'évaluation des risques dus à la pollution de l'environnement sont fort interessants. Quelle sera la liste des priorités qui sera considèrée en ce qui concerne des problèmes à aborder et des populations à étudier?

FOURNIER (France)

Les propositions qui ont été faites tendent surtout à éviter une certaine confusion entre les différents secteurs de toxicologie.

Les problèmes à aborder en priorité dépendent:

- pour la toxicologie sub-aiguë de l'évolution de la technologie industrielle et des produits médicamenteux,

- pour la toxicologie chronique, des produits non dégradables essentiellement d'origine minérale, des produits susceptibles d'un effet cumulatif en particulier cancérogène ou mutagène.

Un échange de vues sera donc nécessaire entre les différents spécialistes de toxicologie afin que les choix portent avant tout sur des produits réellement manipulés ou apparaissant en quantité notable de manière persistante ou encore susceptibles de provoquer des cancers spontanés ou expérimentaux.

Les populations à étudier sont:

- pour la toxicologie subaiguë ceux qui sont particulièrement exposés : ouvriers pour les produits industriels, malades pour les médicaments.

- dans le domaine de la toxicologie chronique des échantillons de population à suivre pendant des périodes suffisamment longues.

METHODOLOGIE POUR L'EVALUATION DE L'EXPOSITION DE L'HOMME RESULTANT DE LA CONTAMINATION DES ALIMENTS PAR LES METAUX LOURDS. ETUDE DE QUELQUES CAS CONCRETS

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RESUME

Dans le cadre d'une Association entre les Communautés Européennes et le CEA, une méthodologie, inspirée par les recherches antérieures dans le domaine radioactif, a été mise au point en vue d'évaluer, dans toute situation, les quantités de métaux lourds ingérées par l'homme en fonction des niveaux dans le milieu, des régimes alimentaires et des caractéristiques des transferts, en tenant compte des concentrations et des dilutions qui peuvent intervenir lors des différents stades du transfert: production, transformation et distribution des aliments. La même méthodologie permet, inversement, de déterminer, dans chaque cas, la capacité limite du milieu. Compte tenu de la complexité des différents paramètres intervenant dans les transferts, des études de sensibilité apparaissent indispensables pour définir les recherches à entreprendre en priorité.

Pour concrétiser les conceptions précédentes, on a appliqué cette méthodologie aux transferts des métaux lourdes (Hg, Cd, Pb, Cu, Zn, en particulier) dans des chaînes alimentaires aquatiques et continentales.

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ABSTRACT

On the basis of previous research in the radioactive sphere, a methodology has been developed by an Association of the European Communities and the CEA, with a view of evaluating quantitatively in any given situation, the heavy metals ingested by man, as a function of levels in the environment, diet and transfer characteristics, and taking into account concentrations and dilutions which may occur at the different transfer stages viz. production, processing and distribution of foodstuffs. Conversely, the same methodology can be used to determine, in each case, the limiting capacity of the environment. Given the complexity of the different parameters occurring during transfer processes, sensitivity studies appear to be essential, in order to define which research should be given priority.

In order to make the previous ideas more concrete, this methodology was applied to the transfer of the heavy metals (especially Hg, Cd, Pb, Cu and Zn) in the food chains, both in water and in the soil.

1. INTRODUCTION

Il est bien connu que les radionucléides rejetés dans le milieu sont susceptibles de parvenir à l'Homme, pour une grande part, par la voie de la chaîne alimentaire. Le cheminement des polluants radioactifs des points de rejet jusqu'à l'organe critique de l'Homme a fait l'objet d'études très poussées, qui ont servi de bases à l'évaluation des niveaux admissibles dans le milieu et à celle des taux maximaux d'introduction des polluants dans l'organisme à partir de la dose maximale admissible pour le groupe de population considéré. Plus généralement, il est possible de relier le niveau x d'un polluant radioactif dans le milieu au débit de dose D délivrée à l'organe critique de l'Homme. Les relations font intervenir les paramètres physiques, chimiques, biologiques, économiques dans les transferts. Les recherches effectuées dans le cadre de l'Association EURATOM-CEA "Niveaux de pollution du milieu ambiant" ont permis de faire l'inventaire de ces paramètres, et, dans divers cas concrets, d'évaluer l'incidence de leur variabilité sur le débit de dose. Ce travail a permis d'éclairer l'importante notion de "capacité radiologique limite "d'un milieu récepteur, en tenant compte des différents stades du transfert: production, transformation et distribution des aliments, diététique (1).

Il est apparu comme souhaitable de s'inspirer de la méthodologie mise au point dans le domaine radioactif en vue de chercher à évaluer, en toutes situations, les quantités de métaux lourds ingérées par l'Homme, en fonction des niveaux dans le milieu. Les exemples qui vont suivre sont empruntés à des études réalisées en collaboration avec l'Association et divers laboratoires.

2. TRANSFERT DU MILIEU AUX PRODUITS BRUTS DE L'ALIMENTATION DE L'HOMME

2.1. Transfert des métaux lourds de l'eau d'irrigation aux végétaux

On a en particulier étudié le transfert du cadmium de l'eau au riz irrigué par submersion, en utilisant des rizières artificielles miniaturisées, au Laboratoire d'Ispra de la Division de Biologie d'Euratom (2). On a constaté que le facteur de transfert F, eau → endosperme, du cadmium

$$\frac{\text{Cd dans l'endosperme}}{\text{Cd dans l'eau d'irrigation}}$$

est de l'ordre de 60, bien supérieur à celui du zinc ($F \approx 8$). Cette expérimentation souligne l'intérêt de recherches sur la contamination de produits céréaliers par le cadmium.

2.2. Transfert des métaux lourds de l'eau aux organismes aquatiques

Une recherche de longue haleine est actuellement poursuivie à Nice au Centre d'Etudes et de Recherches de Biologie et d'Océanographie Médicale (CERBOM) sur le transfert de métaux lourds dans des chaînes trophodynamiques marines. Les éléments sont, comme dans la réalité, introduits sous forme ionique simple et sous forme associée à divers composants organiques naturels et artificiels. Le premier échelon marin est contaminé par l'eau, le second, à la fois par l'eau et le premier échelon qui est consommé comme aliment. Le dernier échelon comporte un mammifère, la souris, considérée comme consommateur final des chaînes trophiques. Le tableau 1 donne un exemple des résultats obtenus sur une chaîne néritique à mollusques (3). Des recherches sont actuellement entreprises à Ispra en vue d'étudier les transferts des métaux lourds (Hg, Cd, Zn, Pb) de l'eau, aux organismes dulçaquicoles (facteurs de transfert)

$$\frac{\text{concentration dans l'organisme (poids frais)}}{\text{concentration dans l'eau}}$$

3. TRANSFERTS DES PRODUITS BRUTS AUX PRODUITS AU STADE DE LEUR CONSOMMATION PAR L'HOMME

Divers aspects ont été envisagés: la transformation et la préparation des denrées alimentaires, les processus de commercialisation et de distribution, enfin des enquêtes sur les régimes alimentaires dans la Communauté Européenne.

3.1. Transferts des produits bruts aux produits au stade de leur consommation par l'Homme

Ces études ont été entreprises en collaboration avec l'Institut National de la Recherche Agronomique, le Ministère de l'Education

TABLEAU I - ORDRE DE GRANDEUR DES FACTEURS DE TRANSFERTS DES METAUX LOURDS DANS UNE CHAINE NERITIQUE A MOLLUSQUES (éléments introduits à l'état ionique simple)

	Cu	Zn	Pb	Cr (VI)	Hg
Phytoplancton	1000	7000	5000	100	3000
Moule	120	1200	150	40	100

TABLEAU II - TAUX DE SECRETION DANS LE LAIT DES ELEMENTS INGERES PAR LA VACHE (rapport des quantités secrétées, par jour et par animal, aux quantités ingérées, par jour et par animal)

Fe : 0,009
Zn : 0,08
Sr : 0,03

Cd : 0,06
Pb : 0,1
Mn : $\leq$ 0,0010

Nationale et le Laboratoire de Biologie Végétale du CEA à Grenoble. On a étudié en particulier les transferts des métaux lourds dans la chaîne: aliment du bétail, lait, produits laitiers: l'expérimentation a montré que , pour tous les éléments envisagés, l'animal consitue un filtre efficace entre la pollution chimique du milieu et le lait (tableau II) (4).

3.2. Commercialisation et distribution

Le mouvement des produits alimentaires, bruts ou transformés, est un paramètre important à prendre en considération, soit qu'il aboutisse à une dilution des produits issus d'une zone susceptible d'être contaminée, soit, au contraire, qu'il aboutisse à une concentration, sur certains marchés, de produits provenant de zones intéressées par des rejets industriels et urbains.

Un modèle permettant d'estimer l'influence des circuits de collecte, de transformation et de distribution des produits alimentaires sur le facteur de dilution d'une contamination intervenant au stade de la production agricole est actuellement à l'étude et sera testé sur des exemples, car il doit être adapté aux problèmes particuliers posés par chacune des grandes catégories de produits alimentaires à l'un ou l'autre des stades de leur cheminement.

En ce qui concerne le stade de la collecte, l'accent a déjà été mis sur les produits céréaliers, notamment le blé et la farine. Il a été montré, par exemple, qu'en France, les zones d'exportation du blé étaient: le Centre (Orléans), la Picardie et la Champagne, les régions importatrices étant les zones urbaines industrialisées; Paris constitue la plaque tournante de la commercialisation de la farine (5). Pour les produits laitiers, on s'appuie sur des études réalisées sous l'égide du Ministère de l'Agriculture (6), fournissant un panorama de l'industrie laitière, qui montre une certaine spécialisation des grandes installations dans tel ou tel type de fabrication, selon la région où elles sont implantées. Pour les mouvements des produits fruitiers et légumiers, des données sont obtenues auprès du Centre Français du Commerce Extérieur.

3.3. Aspects alimentaires et diététiques

Une enquête réalisée par CRESTA dans diverses régions permet de se faire une idée de la variabilité des régimes alimentaires dans les pays de la Communauté Européenne (7). On a constaté que, contrairement peut-être aux macroéléments indispensables, les apports alimentaires relatifs aux oligoéléments indispensables sont relativement peu variables d'une région à l'autre. Mais le problème des éléments polluants reste posé.

Les aspects diététiques n'ont pas pu être abordés par l'Association. Mais le Service de Recherches Toxicologiques et Ecologiques du C.E.A. a entrepris des études expérimentales sur le devenir des radionucléides au cours de la préparation des aliments, recherches dont on peut s'inspirer dans le cas des métaux lourds (8).

4. CONCLUSIONS

Il apparaît très intéressant de poursuivre, dans le même esprit, les recherches encore sporadiques effectuées sur les transferts de métaux lourds. Des modèles inspirés de ceux mis au point dans le cas de polluants radioactifs permettent d'évaluer les quantités D ingérées d'un élément, en l'unité de temps, si on connaît les quantités Qi de chaque vecteur alimentaire i ingéré en l'unité de temps, les facteurs de transfert F_i milieu → aliment et le niveau de contamination χ du milieu:

$$D = \chi \sum_{1}^{n} Q_i \, F_i \quad \text{(n vecteurs alimentaires).}$$

On pourra déterminer le niveau limite χ_ℓ dans le milieu, si on peut apprécier la quantité maximale ingérable D_ℓ. De premières études de sensibilité sur D montrent que les paramètres les plus sensibles sont ceux qui modifient les valeurs des facteurs de transfert, en particulier les paramètres impliqués par la transformation, la commercialisation, la distribution et la préparation culinaire des aliments.

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DISCUSSION

ANDERSON (U.S.A.)

Qu'est-ce qui a produit les facteurs de concentration pour les moules? Etaient-elles exposées à des algues contaminées ou à de l'eau ou aux deux à la fois?

BITTEL (France)

Le phytoplancton a été cultivé dans de l'eau de mer contaminée. Les moules ont été placées, pendant une semaine, dans cette même eau et ont reçu, comme aliment, les micro-algues précédemment contaminées. La contamination des moules est donc à la fois directe, par l'eau, et indirecte, par les aliments.

MERCURY PATHWAYS TO MAN AND "IN VIVO" CONTENT OF THE POPULATION OF THE MT AMIATA AREA

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ABSTRACT

In this paper have been discussed and compared the results referring to the two main routes of Hg intake, inhalation and ingestion, and the average amount due to each route has been estimated.

Furthermore, both the Hg concentrations in some human tissues (blood, hair) and the Hg excretions (urine, feces) from selected subjects have been measured. Such subjects were divided in three groups according to the degree of their exposure to Hg contamination.

In order to assess the ratio between Hg contamination levels in the environment and in man, some correlations have been carried out among the Hg concentrations, found "in vivo" in the various biological samples, and Hg amounts introduced in man through ingestion and inhalation.

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1. Introduction

In a previous paper, Bombace M.A. et al [1], the Hg distribution and environmental concentration have been studied in an area selected owing to both its mineral resources and industrial activity.

In the present paper the study has been mainly focused on some group of human population, exposed to different levels and routes (ingestion and inhalation) of Hg contamination.

Among such groups, those more heavily exposed introduce Hg mainly through inhalation of either Hg vapor (people working near the furnaces where the metallic mercury is extracted) or mineral dust (miners).

In spite of the many papers (Wilcox et al. [2], Dinman [3] Nordberg and Skerfving [4]) dealing with the relationship existing in man between the ingestion of organic mercury and the corresponding level in biological samples (blood, hair, urine), few data (Smith et al. [5]) are available on such relationship due to inorganic Hg contamination from vapor or dust.

The Hg intake due to the environmental exposure has been examinated separately from that due to the working exposure.

A direct assessment of the Hg vapor inhalation due to the professional exposure was not possible; in any case, the Hg concentration in the air, inhaled during the working hours by the subjects employed near the furnaces, has been estimated by applying to the urine and blood Hg concentrations in such subjects, the correlation found by Smith et al. [5].

The subjects of the control group have been selected in order to be exposed to Hg intake from the environment only without any professional exposure.

2. Materials and Methods

The subjects selected for this study were divided into the following groups:

- Group A: seven male individuals (29-54 years aged) working near to the furnaces, where the metallic mercury is extracted; such subjects are those involved in the heaviest professional exposure, owing to the Hg air concentration presumably higher in this point than in any other of the mine.
- Group B: thirteen male miners (40-45 years aged) working at the extraction of the Hg ore. The inhalation exposure to Hg vapor is less for this group than for group A and the main exposure for this group is due inhalation or ingestion of the ore's dust.
- Group C: eight control individuals of both sexes, without any professional exposure, 18-30 years aged, selected among the relatives of the subjects considered in groups A and B.

Blood (10cc), hair (few mg), 24 hours urine and feces samples have been taken from every subject. The total meals eaten by the subjects of groups A and B have been collected during the three days preceding the excretion collection date. Every precaution was taken in order to avoid contamination during samples collection.

Each sample was measured by the non destructive neutron activation analysis method described in a previous paper (Bombace M.A. et al[1]).

The treatment of the samples varied according to their nature. Few grams aliquots of feces were irradiated after a preliminar sterilization* in a gamma irradiation facility (^{137}Cs source); the urine volumes (20 cc) were irradiated without any previous treatment. The blood samples have been separated by means of a centrifugation, in two parts, the serum and the red and white cells, which were directly irradiated "in toto".

The total diets have been homogeneized and sterilized in a gamma irradiation facility as the feces samples, and then liophilized; a small aliquot (2-4 g) was then irradiated. The human hair were irradiated after a careful and repeated washing in aceton and ether.

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*Dose to the samples $\simeq$ 5 MRad

The average Hg inhalation for the control group C, was calculated by estimating the air Hg concentration in the region around the mine, by means of the Pasquill formulas and of the following parameters:

a) the wind rose, referred to the different stability categories, was obtained by analyzing both the anenometers data for the period march-april 1974 and the clouds mass on the site.

b) the main Hg discharge point was the furnaces stack (40 m high).

c) the average Hg discharge from the stack was estimated as 1 mg/sec by means of many different air filtration experiences around the mine plant.

The average air Hg concentration, obtained with such calculation, is clearly referred only to the analysed period, and can be considered as only indicative of the order of magnitude of the yearly average value.

3. Results and Discussion

In table 1 and 2 Hg concentrations in the analyzed samples are reported. The data show a clear correlation of the Hg content with the degree of exposure. As the blood is concerned, the individual Hg concentrations for subjects of group A are much higher than those reported for the normal population by Skerfving [4] and Goldwater et al. [6]; group B on the other hand resulted much less contaminated, with 10 subjects over 13 having Hg blood concentrations less than 5 ppb: such a value can be considered as a limit value for the 75%-77% of the non exposed population (Goldwater et al. [6]; Skerfving [4]).

The blood Hg concentrations found in the groups A subjects can be related to the chemical form of the contaminant: the highest values are, indeed, measured in the serum, with a serum/ red and whith blood cells ration almost equal to a value of 2 (tab.3). Such a result could be attributed either to the high reaction speed of inorganic mercury with the seric proteins

TABLE 1

Hg concentration in blood (ng/ml)

Number of Subjects	Group	Blood		Serum		Red and white cells	
		mean ± S.E.	range	mean ± S.E.	range	mean ± S.E.	range
7	A	59 ± 11	37 ÷ 123	93 ± 27	46 ÷ 256	44 ± 4	32 ÷ 63
13	B	*	<5 ÷ 36	*	<5 ÷ 53	*	<5 ÷ 28
8	C	<5	<5	<5	<5	<5	<5

* 3 samples only with Hg concentrations >5 ng/cc

TABLE 2

Hg concentration in urine, feces and hair

Number of Subjects	Group	urine (ng/ml)		feces (µg/g)		hair (µg/g)	
		mean ± S.E.	range	mean ± S.E.	range	mean ± S.E.	range
7	A	251 ± 41	155 ÷ 426	3.5 ± 1.1	0.6 ÷ 8.9	25.0 ± 6.1	7.6 ÷ 50.0
13	B	4.7 ± 1.8	<1 ÷ 24.8	1.2 ± 0.5	0.07 ÷ 6.0	4.0 ± 0.8	1.4 ÷ 8.8
8	C	3.4 ± 1	<1 ÷ 9.0	0.25 ± 0.07	<0.02 ÷ 0.55	1.8 ± 0.4	0.9 ÷ 4.5

(Guirgis et al. [7]), due to its strong degree of ionization, or to the solubility of the Hg vapor in the lipid fraction (Clarkson et al. [8]). On the other hand, a Hg concentration higher in red and white blood cells than in serum was observed, when organic mercury is introduced through a fish diet, according to Dinman [3] and Skerfving [4]. The subjects of group A have also a much higher urine and hair Hg concentration than the other groups (tab.2); this result is less evident for the Hg concentrations in feces which show an high degree of variability (tab.2).

As the average ratios, reported in table 3 for group A, are concerned, the following considerations can be done:

a) the urine/blood ratio is in good agreement with that reportec by Smith [5] for similarly exposed subjects

b) the hair/blood ration is slightly higher than those (181 + 385) reported by Dinman [3] for subjects exposed to organic mercury, assumed mainly through the diet.

Therefore it could be argued that, exposures to a vapor of metallic mercury produce concentrations in some body tissues, as hair, higher than exposures to organic mercury as considered by Dinman [3]

c) as the ratio between the fecal and the urinary excretion (both as 24 hours total excretion) is concerned, no data are available in literature. The results reported for group A seem to show a fairly similar Hg excretion, through both feces and urines, in case of exposures to a metallic mercury vapor.

Other results reported in table 2 and 3 for the groups B and C show no indication of a pronounced exposure as for group A. On the other hand, the data of group B indicate a certain degree of Hg contamination, probably due to inhalation and/or ingestion of mineral dust: such a contamination, which is poorly metabolized in lungs and in the gastrointestinal tract is displayed by the high Hg level in feces only.

TABLE 3

Group A - Mean values for individual ratios among Hg concentrations in some tissues and excreta

Ratio	Mean ± S.E.	Range
serum/red and white cells	1.97 ± 0.36	1.29 ÷ 4.02
urine/blood	4.40 ± 0.51	3.12 ÷ 7.22
hair/blood	441 ± 110	105 ÷ 940
feces/urine*	1.05 ± 0.16	0.70 ÷ 1.53

* 24 hours fecal and urinary excretion

TABLE 4

Urinary, fecal and total Hg excretion compared with the Hg intake through the diet and the inhalation (μg/day)

Number of Subjects	Group	Urinary excretion		Fecal excretion		Total excretion		Intake		
								Diet		
		mean ± SE	range	mean ± SE	range	mean ± SE	range	mean ± SE	range	Average inhalation
7	A	265 ± 49	149 ÷ 468	332 ± 111	104 ÷ 714	562 ± 132	235 ÷ 1183	25 ± 6	6.3 ÷ 98.2	1000
8	B	6.0 ± 2.8	1.3 ÷ 24.6	66.9 ± 15.8	12 ÷ 130	73 ± 15	14 ÷ 129	25 ± 6	6.3 ÷ 98.2	0,2 *
6	C	3.8 ± 0.8	1.3 ÷ 6.1	21.5 ± 4.3	12 ÷ 34	25.2 ± 3.4	18.2 ÷ 35.3	25 ± 6	6.3 ÷ 98.2	0,2 *

* inhalation due to non-professional exposure.

The hair Hg level for group B are slightly higher than those reported for the non exposed population (Dinman [3], Skerfving [4]), while those for group C are in very good agreement with the normal natural values.

With reference to the Hg introduced through ingestion and inhalation, the following results were obtained:

1) the average amount introduced by any subject through the diet resulted to be 25 μg of Hg per day

2) the inhaled amount due to the environmental exposure, for the population living inside the area of 1 km radius from the stack (almost all the considered subjects are living in that area), resulted to be nearly 0.2 μg of Hg per day (average Hg concentration in air = 10.10^{-3} $\mu g/m^3$; air inhaled during 24 hours = 20 m^3 (ICRP [9]). Such an amount is clearly negligible when compared to that introduced through the diet.

3) the quantity, due to the professional exposure, inhaled by the subjects of group A, was estimated to be 1 mg of Hg per day, on the basis of an air Hg concentration of 0.1 mg/m^3 (air inhaled during 8 hours work day = 10 m^3 (ICRP 9).

Some provisional conclusions can be drawn from the values reported in table 4, as the 24 hours total excretion and the total Hg intake are considered:

1) the main Hg intake for group A subjects is due to the Hg inhaled during working hours, being negligible the contribution due to the diet. Furthermore the Hg inhaled as a vapor is easily metabolized and accumulated in some tissues, the total excretion being less than the total intake (see tab. 4). As a consequence fairly high levels were found for those subjects in blood, urine and hairs.

2) the group B subjects seem to be exposed to a random intake of mineral dust, which, being poorly metabolized in the lungs and in gastrointestinal tract, are more easily excreted through the feces. For such a reason the feces/urine

ratio for this group is higher than that found in other groups. The dietary Hg intake for group B is not as negligible as for group A.

3) a substantial equilibrium between total intake (mainly dietary) and total excretion has been found for group C subjects. As a consequence the Hg levels in the body tissues of this group are fairly identical to those found in the normal population

4) the feces/urine ration is function of the kind of exposure; such a ratio reaches a value of 10 in group B; it is lower in group C than in group B by a factor of 2, and finally lower by a factor of 5 in group A than in group C.

In any case it has to be considered that all the average data reported in tab.1-4 are mainly indicative of the order of magnitude, due to both the poor number of subjects examined and the individual variability of the analyzed quantities; for such a reason in any table the range of such quantities is also reported.

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ACCUMULATION AND RELEASE OF PETROLEUM HYDROCARBONS BY EDIBLE MARINE ANIMALS

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ABSTRACT

The objectives of this investigation were to determine the petroleum hydrocarbon composition of the tissues of oil-exposed marine animals and to determine the rates of petroleum hydrocarbon release when animals were returned to oil-free sea water.

When exposed to dispersed #2 fuel oil in sea water, oysters rapidly accumulated a wide spectrum of different hydrocarbons. The mono- di- and tri-methylnaphthalenes were accumulated to higher concentrations in the oyster tissues than were the other di- and tri-aromatic hydrocarbons or individual paraffins. When oysters were returned to oil-free sea water, they released 90% of the accumulated paraffins in 24 hours. Naphthalenes were released to background levels in 28 days.

When exposed to water-soluble fractions of #2 fuel oil, clams, shrimp and fish rapidly accumulated naphthalenes in their tissues to levels one or more orders of magnitude higher than the exposure concentrations. When returned to oil-free sea water, they released the naphthalenes to low or undetectable levels in from 6 to 14 days.

These results are discussed in relation to the potential health hazards arising from the consumption of oil-contaminated marine animals.

1. Introduction

Pollution of the marine environment by petroleum and petroleum hydrocarbons (PHCs) may pose a health hazard to consumers of fish and shellfish products. Petroleum is a complex mixture of thousands of different hydrocarbons (HCs) and related substances, some of which are known to be highly toxic and/or carcinogenic. Several investigations have shown that when marine animals are exposed to oil-contaminated sea water they rapidly accumulate PHCs in their tissues, often to levels many times higher than those in the exposure water. Blumer *et al*. [1] reported that oil-contaminated oysters, *Crassostrea virginica*, retained the accumulated PHCs in their tissues permanently. However, more recently it has been shown that when oil contaminated oysters *C. virginica* (Stegeman and Teal, [2]) or mussels *Mytilus edulis* (Clark and Finley, [3]) were placed in oil-free sea water, they rapidly released the accumulated HCs. Little information was provided by these investigators concerning the PHC composition of the tissues of oil-exposed animals. Such information is essential in predicting potential health hazards arising from the consumption of oil-contaminated marine animals. An investigation was therefore initiated dealing with the PHC composition of oil-exposed marine animals and the relative rates of release of different PHCs when the animals were returned to oil-free sea water.

2. Methods and Results

A group of oysters was exposed to dispersed #2 fuel oil in a 46 l flow through exposure tank for 8 hours. The dispersed oil reached a concentration of approximately 400 ppm in the aqueous phase of the exposure tank. After the exposure period 3 oysters were sacrificed and their soft tissues pooled for HC analysis. The remaining oysters were placed in large aquaria containing filtered oil-free sea water. At different time intervals up to 672 hours (28 days) 3 of these oysters were sacrificed for tissue hydrocarbon analysis. Unexposed oysters from the same population were also analyzed to ascertain the background levels of PHCs present. Quantitative determinations of tissue PHCs were conducted by gas chromatographic mass spectrometric methods (Warner, [4]). The results of this experiment are summarized in Table I. The unexposed oysters contained a total of 2.4 ppm of naphthalene and alkylnaphthalenes, the di- and tri-methylnaphthalenes being the dominant forms present. After 8 hours exposure to dispersed #2 fuel oil, the animals had accumulated a total of 312 ppm

Table I. Concentrations of different petroleum hydrocarbons in the tissues of oysters *Crassostrea virginica* after 8 hours exposure to a #2 fuel oil-in-water dispersion and at different times following return to oil-free sea water.

Time	Petroleum Hydrocarbon Concentration (ppm, µg/g wet wt.)														
(hours)	n-P	N	1-MN	2-MN	DMN	TMN	B	MB	F	MF	DBT	P	MP	DMP	Total
Exposure															
0	---	0.2	0.1	0.3	1.0	0.8	---	---	---	---	---	---	---	---	2.4
8	235	14.7	8.7	15.0	21.8	9.1	0.3	0.5	1.0	1.2	0.3	1.9	1.9	0.3	312
Depuration															
3	136	12.0	8.4	12.0	22.7	10.8	0.3	0.4	0.7	0.7	0.3	1.3	1.3	0.2	228
6	68	7.3	5.1	7.3	13.2	5.7	0.1	0.2	0.4	0.2	0.1	0.6	0.6	0.1	109
24	18	6.5	5.7	7.6	14.8	9.5	0.2	0.2	0.5	0.7	0.2	1.2	1.3	0.3	67
120	10	8.2	4.7	6.8	13.4	4.9	0.1	0.1	0.2	0.1	0.1	0.4	0.4	0.2	54
672	---	---	---	0.1	0.5	0.9	---	---	---	---	---	---	---	---	1.5

*n-P, n-paraffins; N, naphthalene; 1-MN, 2-MN, 1 methyl- and 2-methylnaphthalene; DMN, dimethylnaphthalene; TMN, trimethylnaphthalene; B, biphenyl; MB, methylbiphenyl; F, fluorine, MF, methylfluorine; DBT, dibenzothiophene; P, phenanthrene; MP, methylphenanthrene; DMP, dimethylphenanthrene.

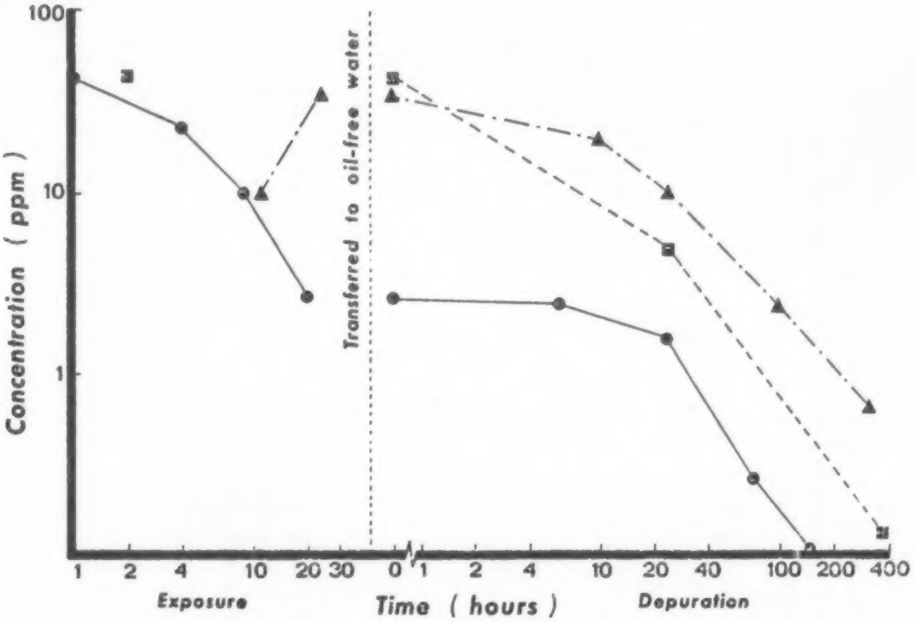

Figure 1. The concentrations of total naphthalenes (TNs) in the tissues of clams, shrimp and fish at different times during exposure to water-soluble fractions of #2 fuel oil and following return to oil-free sea water.

▲—·—▲ Clams, Rangia cuneata, exposure concentration 3.4 ppm TNs.

●——● Shrimp, Penaeus aztecus, exposure concentration 0.7 ppm TNs.

■---■ Fish, Fundulus similus, exposure concentration 1.9 ppm TNs.

of PHCs in their tissues. The dominant HC type present at this time was the normal paraffins. These were represented on the gas chromatogram by a large unresolved envelope and a series of resolved peaks representing the C_{12}-C_{23} series of n-paraffins. The dominant resolved n-alkane present was n-pentadecane (5.4 ppm). The different naphthalenes were present at concentrations ranging between 8.7 and 21.8 ppm while the other di- and triaromatic HCs were present at much lower concentrations.

When the oysters were returned to oil-free sea water they rapidly released their accumulated oil HCs. More than ninety percent of the n-paraffins were released in 24 hours. The aromatic HCs were released much more slowly. From 24 to 672 hours the naphthalenes were the dominant HCs present in the oyster tissues. After 672 hours of depuration only small amounts of mono-, di- and tri-methylnaphthalenes remained. In similar experiments with other marine species and with three other oils, South Louisiana crude, Kuwait crude and Venezuelan bunker C, the pattern of hydrocarbon uptake and release was similar to that described above. In all cases, naphthalenes were accumulated to high concentrations by the organisms and were retained longer than other aromatics or paraffins.

These results indicate that the concentration of total naphthalenes (TNs) can be used as an indicator of petroleum contamination of marine animals. In subsequent experiments, accumulation and release of TNs by clams, shrimp and fish were investigated. An ultraviolet spectrophotometric method for the determination of tissue naphthalenes was used (Neff and Anderson, in preparation).

Groups of clams, Rangia cuneata, brown shrimp Penaeus aztecus and fish Fundulus similus were placed in synthetic sea water containing different concentrations of the water-soluble fraction of #2 fuel oil. The animals were exposed to the water-soluble fraction for 2 to 24 hours and then placed in oil-free sea water. At different time intervals during and after exposure some animals were sacrificed and the concentration of TNs in their tissues was determined (Figure 1).

The patterns of uptake, retention and release of TNs were somewhat different for the three species of animals examined. The shrimp accumulated TNs extremely rapidly. The maximum concentration of TNs (43 ppm) was reached after only one hour of exposure. The shrimp then began to release the accumulated compounds back to the exposure water. The clams accumulated the materials more slowly but continued to do so at a relatively constant rate for the 24 hour period. In 24 hours the clams accumulated an average of 34 ppm TNs in their tissues. During the 2 hour exposure period to a #2 fuel oil water-soluble fraction, the fish accumulated TNs very rapidly to average levels of 43.2 ppm. In all three cases the maximum tissue concentration was one or more orders of magnitude higher than that of the exposure water.

When returned to oil-free sea water, all three species rapidly released the accumulated TNs from their tissues. The fish and shrimp released the PHCs much more rapidly than did the clams. All three species were able to reduce tissue naphthalenes to low or undetectable levels within 14 days.

In subsequent experiments clams and fish were shown to completely depurate accumulated hydrocarbons within 3 to 4 weeks.

3. Conclusions

When marine animals are exposed to oil-contaminated sea water, they rapidly accumulate a wide variety of different petroleum hydrocarbons in their tissues. The mono- di and tri-methylnaphthalenes are the individual petroleum hydrocarbons accumulated to the highest concentration in all species and with all the oils so far tested. These are also the PHCs retained for the longest time when the animals are returned to oil-free sea water. However, these aromatic hydrocarbons are released, reaching undetectable levels within 2 to 4 weeks. The pattern of uptake, retention and release of the carcinogenic HC, benzo[a]pyrene, has been shown to be similar to that of the TNs in clams (Anderson *et al*., unpublished observation), mussels (Lee *et al*., [5]) and fish (Lee *et al*., [6]).

Naphthalenes have also been shown to be the most toxic component of oil to marine animals (Anderson *et al*., [7]) and are known to have substantial human toxicity (Gerarde [8]). Since marine animals would be expected to accumulate these HCs to very high levels following an oil spill, consumption of recently contaminated marine animals could pose a health hazard to man. However, rapid release of these compounds from marine animals probably also takes place in the natural environment, rendering the animals fit for human consumption after a relatively short period of time. The rapid release of accumulated hydrocarbons by marine animals also indicates that under natural conditions, food chain accumulation of PHCs would not occur. This conclusion is supported by the observation of Burns and Teal [9], that there was no relationship between tissue PHC concentration and trophic level among marine animals in the *Sargassum* community.

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DISCUSSION

PICHE (Canada)

Has Dr. Anderson investigated the nature of the depuration process which he described? Is it the result of a simple washing out or rather through assimilation and conversion to other forms in the metabolism of the organisms studied?

ANDERSON (U.S.A.)

In fish (Lee et al., 1972) and more recently in crabs (Corner et al., 1974) the metabolic break-down of naphthalenes has been demonstrated. In molluscs this conversion has not been found and the longer time to complete depuration by these animals may indicate that "washing out" is the only mechanism available.

PACKHAM (U.K.)

Has any work been done on the tainting of the organisms as a result of fuel oil contamination? Is there any evidence that a dangerous degree of contamination would make the organism inedible?

ANDERSON (U.S.A.)

Several of us in the US working with hydrocarbons and marine animals have considered conducting a study relating chemical analyses of tissues to animals selected as being tainted by a taste panel. Persons experienced in this type of study tell me that there is considerable variability between the hydrocarbon taste capabilities of individuals. I would estimate that most individuals could detect levels between 0.5ppm and 1.0ppm of these aromatic compounds (naphthalenes).

LAO (Canada)

1. What is the concentration level of BaP that you found in the sample?

2. Could you describe the analytical technique (e.g. GC conditions) you use for determining hydrocarbons.

ANDERSON (U.S.A.)

I should have noted that our studies with BaP utilized C^{14} - labelled material and therefore all data were derived from analyses of radioactivity. The clams were exposed to a concentration of 0.030 ppm and attained levels of approximately 3 ppm. We observed a constant decrease in tissue levels of animals maintained in clean sea water. The radioactivity reached background levels at about 48 days. It would be well to verify radioactivity data with chemical analyses, but as you know, these determinations are extremely expensive and time consuming.

BITTEL (France)

Can a correlation be established between the accumulation of petroleum products in molluscs and the amount of fatty matter they contain?

ANDERSON (U.S.A.)

We have not correlated lipid content of our animals with the levels of accumulated hydrocarbons. From the study by Stegeman and Teal (1973) there does appear to be a relationship between the maximum extent of accumulation in oysters and their lipid content. In their study the oil was supplied over a period of 50 days, while our exposures were quite short-term (hours). To control for differences in lipid content and reproductive state all animals used in a given experiment are collected from the field at the same time. It is possible that individual differences in the hydrocarbon content of exposed bivalves may be due to variations in lipid content, but on short exposures the amount of time spent open and filtering is perhaps more important.

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MODELLE
MODELS
MODELES
MODELLI
MODELLEN

Vorsitzender - Chairman - Président - Presidente - Voorzitter

B. PRINZ
(Bundesrepublik Deutschland)

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NONLINEAR MODELS IN MULTIVARIATE ANALYSIS APPLIED IN EXPOSURE ASSESSMENT

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Prague

ABSTRACT

In the analysis of data on human exposure to environmental pollutants there is a need for techniques seeking a solution between a set of input variables and a categorized dependent variable (e.g. health effects). If the dependent variable is stochastic, we are concerned with its expectation as a function of the variables defining the conditions. We restrict ourselves to the polynomial response surface $y = (X_1,\ldots,X_q)$ *and find the estimates of the parameters of the model. Furthermore an estimate of the variance is obtained and the adequacy of the model is tested.*

Experimental designs from which the coefficients of the model can be estimated are discussed and their standard forms are shown. It is emphasized that we need not limit ourselves to designs that are simple factorial and that we can use replicate results only for some sets of the input variables to obtain an unbiased estimate of the residual variance.

Two or more designs can be compared by comparing the accuracy of estimation of $(X_1,\ldots,X_q)$ *expressed by the variance of the estimator. The comparison is sometimes simplified by the use of rotatable designs, in which the variance of the estimator depends only on the "distance" of the point* $(X_1,\ldots,X_q)$ *from the centre of the design.*

The response model will be illustrated on examples of medical examinations in selected groups of population.

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1. Introduction

The exposure-effect relationships offer the applications of a variety of statistical methods. Some of them require the use of the technique of random processes while others can be plausibly expressed by the adoption of suitable methods of statistical multivariate analysis.

This paper is aimed at models with a set of explanatory environmental variables such as climate conditions, age, sex, education, housing, social conditions etc. available for the exploitation of multivariate data. Appropriate analysis is applied once the mathematical model for the data has been specified.

2. The Theory

2.1 The Response Surface

The model used is

$$y_i = \beta_o + \sum_{j=1}^{q} \beta_j x_{ji} + D_i + z_i \quad /i=1,2,\ldots,p/$$

where $/x_{1i},x_{2i},\ldots,x_{qi},y_i/$ represent the values of q "independent" defining variables $x_1,x_2,\ldots,x_q$ and one "dependent" stochastic variable y_i for the i-th individual in a random sample of size p. The z_i's are assumed to be mutually independent and normally distributed random variables with expected value zero and variance σ^2. The β's are unknown constants. The parameters D_i account for any departures from linearity. In order to be able to test whether the D_i's are zero we have to obtain an unbiased estimate of σ^2. This can be done only if we have available more than one observation y_i for at least one set of values of the controlled variables $x_{1i},\ldots,x_{qi}$. Thus we have the modification of our model

$$y_{ik} = \beta_o + \sum_{j=1}^{q} \beta_j x_{ji} + D_i + z_{ik} \quad \begin{array}{l}/i=1,2,\ldots,p;\\ k=1,2,\ldots,n_i/\end{array}$$

with at least one n_i greater than 1. We can introduce $N=\sum_{i=1}^{p} n_i$.

Then the mean is

$$\bar{y}_{i.} = \beta_o + \sum_{j=1}^{q} \beta_j x_{ji} + D_i + \bar{z}_{i.}$$

and so

$$y_{ik} - \bar{y}_{i.} = z_{ik} - \bar{z}_{i.}$$

Since the difference $y_{ik} - \bar{y}_{i.}$ is expressed without rest in terms of the errors z's, the "Within Arrays" mean square

$$(N - p)^{-1} \sum_{i=1}^{p} \sum_{k=1}^{n_i} (y_{ik} - \bar{y}_{i.})^2$$

can serve as an unbiased estimator of σ^2 having /N - k/ degrees of freedom.

The remaining "Between Arrays" sum of squares can be split into two parts, one that is due to multiple linear regression and one that reflects the departure from linearity with q and /p-q-1/ degrees of freedom respectively. The ratio of the latter and the "Within Arrays" mean square is used for the test of the existence of the D_i's and is compared with the critical values of the F-distribution with (/p-q-1/,/N-p/) degrees of freedom.

In most cases of estimating health effects of environmental pollution we can restrict ourselves to the model when y_i is a polynomial in the x's not proceeding beyond the terms of second order. Such a model can be written as

$$y_{ik} = \beta_o + \beta_1 x_{1i} + \dots + \beta_q x_{qi} + \beta_{11} x_{1i}^2 + \dots + \beta_{qq} x_{qi}^2 + $$
$$+ \beta_{12} x_{1i} x_{2i} + \dots + \beta_{q-1,q} x_{q-1,i} x_{qi} + z_{ik}$$

with $i=1,2,\dots,p; k=1,2,\dots,n_i$ /$n_i > 1$ for at least one i/.

Since the x's are controlled variables we will treat the model with the technique of multiple linear regression. In the appropriate analysis of variance the ratio of

$$\left[p - \frac{1}{2}(q+1)(q+2)\right]^{-1} \cdot \sum_{i=1}^{p} n_i (\bar{y}_{i.} - b_o - b_1 x_{1i} - \dots - b_{q-1,q} x_{q-1,i} x_{qi})^2$$

to the "Within Arrays" mean square is used as an F-test for the adequacy of the model./ b_i and b_{ij} are the fitted values of β_i and β_{ij}; the coefficient at the sum is calculated as $p - \left[1 + q + q + \frac{1}{2}q(q - 1)\right]$. Obviously p has to be greater than $\frac{1}{2}(q+1)(q+2)$./

2.2 The Experimental Design

Our model can be considered as a second-order design for which it is possible to obtain the estimates of the β's. A 3^2 complete factorial is such a design /Cochran and Cox [1]/ and the terms $\beta_j x_{ji}$ and $\beta_{jj} x_{ji}^2$ correspond to linear and quadratic main effects of the j-th factor while the term $\beta_{jm} x_{ji} x_{mi}$ corresponds to the interaction between the j-th and m-th factors.

The estimators of the coefficients and their variances simplify by appropriate linear scaling of the controlled variables if the levels of the factors are equally spaced.

It should be noted that we are not bounded to designs that are simple complete factorials. If we admit the equally spaced levels of the controlled variables, we need not have the identical number of replications at each level. For example, we can extend the design by adding two or more observations at the point around which the design is centered. We can then use these replications to provide an unbiased estimate of σ^2 and to test the adequacy of the model.

In assessing experimental designs for fitting response surfaces we are interested in the accuracy of estimation of the expected values of the dependent variables y_i. It is natural to measure it by the variance of the estimators

$$\tilde{y}_i/x_1,\ldots,x_q/ = b_o+b_1x_{1i}+\ldots+b_qx_{qi}+b_{11}x_{1i}^2+\ldots+b_{q-1,q}x_{q-1,i}x_{qi}$$

This is a function, $V/x_1,\ldots,x_q/$, say, of $x_1,\ldots,x_q$. Its form depends on the experimental design. Two or more designs can be compared by means of this function. This comparison is sometimes simplified by the use of rotatable designs for which $V/x_1,\ldots,x_q/$ is a function of $\sum_{j=1}^{q} x_j^2$ only, i.e. it depends only on the "distance" of the point $/x_{1i},\ldots,x_{qi}/$ from the centre of the experiment. It is useful to have such designs available /Box [2]/.

For second-order designs with two factors the rotatability is achieved by arranging the experimental points in the vertices of a regular polygon centered around the origin (0,0) and at this origin /at least two observations here/. Apart from these designs there are rotatable designs with equally spaced points on each of two circles centered at the origin. The radii of the circles have to be in definite ratios /depending on the numbers of the points on each circle/ for the designs to be also orthogonal /in the sense of providing uncorrelated estimators of the regression coefficients/. These values can be found in Box and Hunter [3].

It can be shown that in the general case a completely balanced rotatable design of second order can be constructed using the following combinations of values of q controlled variables /again the centre of the design is at the origin/. First we take all 2q points with coordinates /$\pm c,0,..,0$/, /$0,\pm c,0,..,0$/,...,/$0,0,..,\pm c$/. Then we add the 2^q points /$\pm d,\pm d,..,\pm d$/ to these points. The constants c and d are chosen so that

$$\frac{c}{d} = 2^{\frac{q}{4}}$$

These designs do not provide an estimate of residual variance unless at least two observations are added, corresponding to values of the controlled variables at the origin /0,0,..,0/.

3. The Data

The response model will be illustrated on examples of various medical examinations. The complete data cannot be shown here for the limited space of the manuscript.

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DISCUSSION

JACOBSEN (U.K.)

Have I understood correctly that your model pre-supposes that the explanatory, "independent" variables are subject to control?

If so, does this not imply that the model is irrelevant to most situations in environmental health research, where the hypothesised explanatory variables are, characteristically not subject to control by the experimenter?

STEPANEK (C.S.S.R.)

In environmental health research we encounter both situations, those with controlled explanatory variables and those lacking the control. My model is of course applicable only in the first case, which is clearly stated in the assumptions made in the first section of the paper. This is applicable to all methods of those fields of multivariate analysis I tackled in my paper.

The situations, in which the model can be adopted, are frequent in the studies on exposure-effect relationships and are mentioned in the paper.

In the other case of uncontrolled stochastic variables an approach using methods of structural analysis is required but we are mostly limited to the linearity of the models.

A LABORATORY MODEL SYSTEM FOR THE STUDY OF THE ACCUMULATION OF CHEMICALS IN THE AQUATIC FOOD CHAIN, EXEMPLIFIED ON α-HEXACHLOROCYCLOHEXANE

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ABSTRACT

The accumulation and elimination behaviour of α-hexachlorocyclohexane (HCH) was studied on a laboratory scale food chain model, consisting of an alga-species (Chlorella pyrenoidosa), a crustacea-species (Daphnia magna) and a fish-species (Lebistes reticulatus, or "guppy"). The direct accumulation by these species from the water was studied as well as the accumulation through the food chain.

Accumulation and elimination took place within 96 hrs for all three organisms tested; from water with low concentrations of α-HCH accumulation took place even more quickly, viz. in 3 hrs.

Accumulation factors (defined as $\frac{\text{concentration in the organism}}{\text{concentration in the water}}$*) ranged from 60 to 350. The accumulation factors were concentrationdependent for the daphniae and the guppy's where higher accumulation factors were found for higher concentrations of α-HCH. These concentrations were close to the* EC_{50}*-values (based on paralysis and mortality) found for these organisms. The accumulation factor was independent on the α-HCH concentration for chlorella, for which organism no* EC_{50}*-value could be established (i.e. 10ppm, the solubility of α-HCH in water).*

The reproduction study with daphniae gave the most sensitive response: this was used to come to a proposed ecological limit for -HCH, which limit frequently is exceeded in Dutch surface waters.

Introduction

Accumulation of persistent chemicals in the food chain is an important factor in the evaluation of potential hazards to men caused by the presence of such chemicals in the environment. In order to efficiently study this accumulation, model systems on laboratory scale must be developed which give indications on the accumulating properties of a given chemical, so that, with due precautions, an estimate can be made of the consequences if that chemical (deliberately or not) is allowed to come into the environment.

The ultimate aim of the study is the development of standard test methods for the evaluation of the environmental hazard of substances, as is required more and more in national and international legislation.

In this paper a relatively simple fresh water[*] model system is described, viz.:

$$\begin{tikzcd}
\text{Chlorella pyrenoidosa} \arrow[d, "(4)"] \arrow[r, shift left, leftarrow] \arrow[r, shift right, "(1)"'] & \text{water} \\
\text{Daphnia magna} \arrow[d, "(5)"] \arrow[r, shift left, leftarrow] \arrow[r, shift right, "(2)"'] & \text{water} \\
\text{Lebistes reticulatus} \arrow[r, shift left, leftarrow] \arrow[r, shift right, "(3)"'] & \text{water}
\end{tikzcd}$$

(the numbers in this scheme refer to the paragraphs (1) to (5) in the Experimental Part, Section I).

As a model substance α-hexachlorocyclohexane was chosen, as little was known about this substance in literature and as its behaviour was already being investigated in our Laboratory on pigs and rats. Furthermore, the substance is frequently found in concentrations of 0.1 - 0.5 micrograms per liter (ppb) in the Rhine river and its tributaries (Greve [1]).

EXPERIMENTAL

SECTION I: ACCUMULATION AND ELIMINATION STUDIES

(1) Water $\leftrightarrows$ Chlorella

Accumulation

Samples of ca 10^9 cells in 100 ml were exposed to three different concentrations of α-HCH, viz. 0.01, 0.05 and 0.80 ppm[**]. After 15, 30 and 180

---

[*] A similar model system can be given for salt water. This system will not be discussed here in order to keep the paper in the limits required.

[**] The solubility of α-HCH is 10 ppm at 22°C, which temperature was also maintained during the accumulation and elimination studies.

minutes the cells were collected by centrifuging during 5 minutes at 3000 rev./min. and analyzed for α-HCH by GLC after extraction with acetone/ petroleum-ether and subsequent clean-up over alumina.
The results are summarized in fig. 1.

From this figure it can be derived that the average accumulation factor ($= \frac{\text{concentration in the algae}}{\text{concentration in water}}$) is about 200 (153-267). If the cytoplasma is separated from the cell walls with the aid of an X-presser the concentrations of α-HCH in these fractions have the ratio 6 : 1. As the ratio of the fat content in these fractions can be calculated to be about 2.5 : 1 (Northcote e.a. [2] and Lewin [3] there seems to be a preference for accumulation in the cytoplasma, rather than in the cell wall. This would indicate not only adsorption, but also absorption.

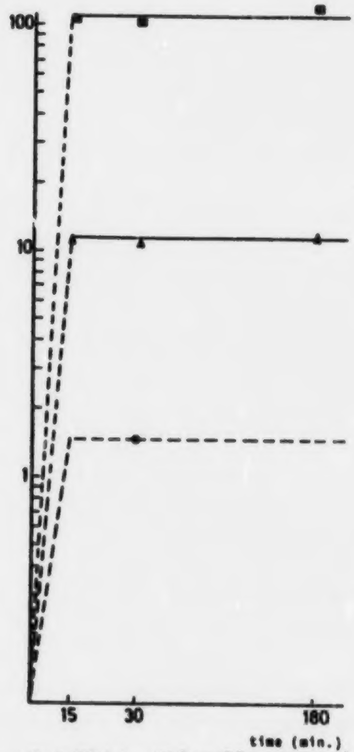

Fig. 1 Accumulation of α-HCH by Chlorella pyrenoidosa from water with different concentrations of α-HCH

- ■ concentrations in the algae after exposure to water with 0.80 ppm α-HCH
- ▲ idem with 0.05 ppm α-HCH
- ● idem with 0.01 ppm α-HCH

Elimination

After having reached the equilibrium levels the algae were transferred into fresh water in order to study the elimination pattern. After 15, 30 and 180 minutes the algae were collected again and analyzed. The water was also analyzed: 90% of the original amount of α-HCH was recovered indicating a negligible decomposition during the experiment.

The results are summarized in fig. 2. From fig. 1 and 2 it can be derived that both accumulation and elimination take place within 15 minutes.

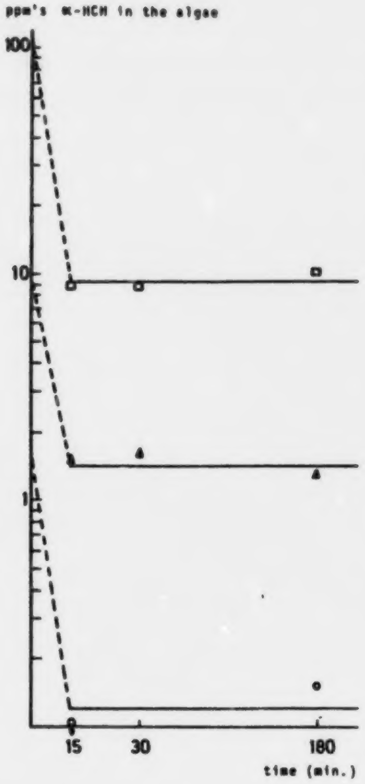

Fig. 2 Elimination of α-HCH by Chlorella pyrenoidosa contaminated with different concentrations of α-HCH into fresh water

□ concentrations in the algae after transfer into fresh water; starting concentration 110 ppm (cf Fig. 1: ■)

△ idem; starting concentration 11 ppm (cf Fig. 1: ▲)

○ idem; starting concentration 1.5 ppm (cf Fig. 1: ●)

(2) Water $\leftrightarrows$ Daphnia

Accumulation

Samples of ca 500 animals (1 week old) in 10 liter were exposed to the same concentrations of α-HCH as mentioned above. Each experiment was carried out in duplicate. After 3, 24, 48 and 96 hrs (or more often if desired) the animals were collected and analyzed for α-HCH. The concentration of α-HCH had to be kept constant by transferring the animals into fresh solutions of α-HCH every 48 hrs, as by that time the concentration of α-HCH had dropped to about 80% of the original value because of the volatility of α-HCH.

The results are summarized in fig. 3.

From this figure an accumulation factor ($= \frac{\text{concentration in daphniae}}{\text{concentration in water}}$) of about 60 can be derived for the 0.01 and 0.05 ppm dosages; for the 0.80 ppm dosage however this factor is about 350. This could possibly be interpreted as a beginning intoxication unabling the animal to "keep out" the α-HCH. This is supported by the acute-toxicity study (section II) where 0.80 ppm was found to be the EC_{50}-value on mortality and paralysis.

From fig. 3 it can also be seen that the equilibrium level was reached in 3 hrs for the lower dosages, but after 48 hrs only for the highest dosage.

Elimination

After having reached the equilibrium levels the animals were transferred into fresh water. After 3, 24, 48 and 96 hrs the animals were collected and analyzed, as was the water. 95% of the original amount of α-HCH was recovered, so that also in this experiment practically no α-HCH was lost.

The results are also summarized in fig. 3.

(3) Water $\leftrightarrows$ Guppy

Accumulation

Samples of 125 fishes (3 weeks old) in 10 liter were exposed to the same concentrations of α-HCH as mentioned in (1). Each experiment was carried out in duplicate. After 0.5, 3, 24, 48 and 96 hrs 20 animals were collected and analyzed for α-HCH. The concentrations of α-HCH had to be kept constant by transferring the animals into fresh solutions of α-HCH every 48 hrs.

The results are summarized in fig. 4.

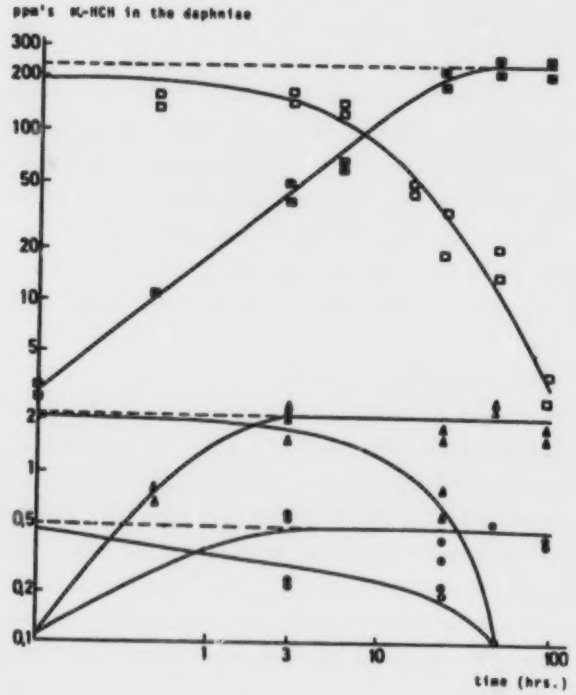

Fig. 3 Accumulation and elimination of α-HCH by Daphnia magna

accumulation:

- ■ concentrations in the daphniae after exposure to water with 0.80 ppm α-HCH
- ▲ idem with 0.05 ppm α-HCH
- ● idem with 0.01 ppm α-HCH

elimination:

- □ concentrations in the daphniae after transfer into fresh water; starting concentration 230 ppm
- △ idem; starting concentration 2.0 ppm
- ○ idem; starting concentration 0.5 ppm

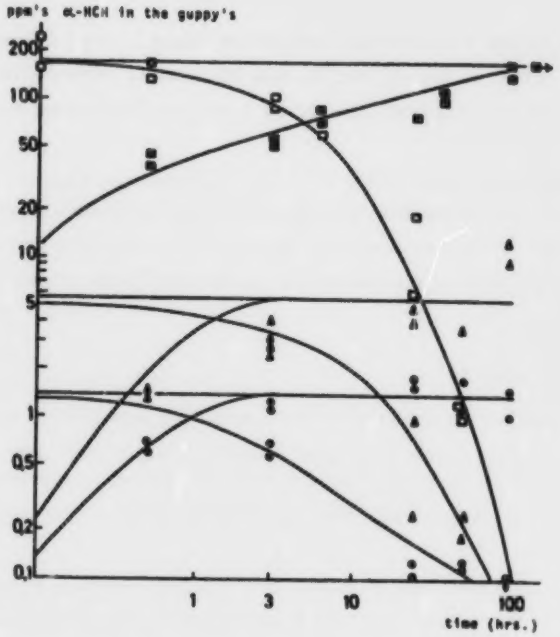

Fig. 4 Accumulation and elimination of α-HCH by guppy's

accumulation:

■ concentrations in the guppy's after exposure to water with 0.80 ppm α-HCH

▲ idem with 0.05 ppm α-HCH

● idem with 0.01 ppm α-HCH

elimination:

□ concentrations in the guppy's after transfer into fresh water; starting concentration 160 ppm

△ idem; starting concentration 5.4 ppm

○ idem; starting concentration 1.4 ppm

From this figure an accumulation factor ($= \frac{\text{concentration in the guppy}}{\text{concentration in water}}$) of about 140 can be derived for the 0.01 and 0.05 ppm dosages; for the 0.80 ppm dosage however this factor is about 250. Also here therefore a tendency to higher accumulation factors can be observed when the concentrations applied come close to acute-toxic levels (cf (2) and section II).

Elimination

After having reached the equilibrium levels the guppy's were transferred into fresh water. After 3, 24, 48 and 96 hrs 20 animals were collected and analyzed. 98-100% of the original amount of α-HCH was recovered from the water.

The results are also summarized in fig. 4. From this figure it can be derived that during the accumulation experiment the equilibrium level was reached in 3 hrs for the lower dosages, but after 96 hrs only for the highest dosage level. Also the elimination took place more slowly at the highest dosage level.

(4) Chlorella ——> Daphnia

Chlorella's were exposed to water with 0.01 and 0.05 ppm α-HCH; these algae were fed to daphniae which were kept in solutions of the same concentrations. The control group was fed with algae which were not equilibrated with α-HCH in beforehand. The equilibrium levels were reached in 3 hrs.

The results are summarized in table I. From this table one can see that the levels in the daphniae fed with contaminated algae were only somewhat higher than in the control group. These results are not unexpected , as the non-contaminated algae will accumulate within 15 minutes their equilibrium-amount of α-HCH, so that effectively the "control" daphniae were also fed with contaminated algae.

(5) Daphnia ——> Guppy

Young daphniae of contaminated parents, which had reached their equilibrium levels after exposure to 0.01 and 0.05 ppm, were fed to guppy's (3 weeks old). The concentrations of α-HCH in the water in which the animals were kept were also 0.01 and 0.05 ppm. The equilibrium levels in the guppy's were reached in 24 hrs.

The results are summarized in table II. From this table a clear difference in equilibrium levels can be seen between the guppy's fed with contaminated and non-contaminated food (the levels in the guppy's fed with contaminated daphniae is 3-4 times higher!). In this respect therefore the guppy shows another accumulation behaviour than the daphnia (4).

The control fishes were fed with Tetramin, which food was experimentally proven not to accumulate any α-HCH.

TABLE I

Accumulation of α-HCH by daphniae fed with contaminated (respectively non-contaminated) algae and kept in solutions with two different concentrations of α-HCH (average concentrations in the daphniae given ± the standard deviation; n = 8)

concentration of α-HCH in water:	0.01 ppm	0.05 ppm
Daphniae fed with:		
contaminated algae	0.68 ± 0.17 ppm	3.2 ± 0.6 ppm
non-contaminated algae	0.50 ± 0.13 ppm	2.2 ± 0.5 ppm

TABLE II

Accumulation of α-HCH by guppy's fed with contaminated (respectively non-contaminated) food and kept in solutions with two different concentrations of α-HCH (average concentrations in the guppy's given ± the standard deviation; n = 6)

concentration of α-HCH in water:	0.01 ppm	0.05 ppm
Guppy's fed with:		
contaminated algae	5.4 ± 0.6 ppm	27.0 ± 3.2 ppm
non-contaminated food *	1.4 ± 0.3 ppm	6.2 ± 3.5 ppm

TABLE III

Summary of the toxicological data on α-HCH determined in the study

organism	parameter	criterion	average value found with 95%-confidence limits	time of exposure
Chlorella pyrenoidosa	EC_{50}	growth	> 10 ppm[a]	48 hrs
Daphnia magna	EC_{50}	mortality + paralysis	1.0 (0.8 - 1.2) ppm	48 hrs
	EC_{50}	reproduction	0.10 (0.05 - 0.19) ppm	12-21 days
Lebistes reticulatus	EC_{50}	mortality + paralysis	0.8 (0.6 - 1.2) ppm	48 hrs

[a] The solubility of α-HCH in water under the circumstances of the experiment is 10 ppm.

* As food Tetramin was used which proved to accumulate no αHCH

SECTION II: ACUTE AND SEMICHRONIC TOXICITY TESTS

Apart from accumulation and elimination studies, toxicological tests were carried out in order to evaluate the ecological effect of α-HCH.

Acute (48 hrs) tests were carried out with Chlorella, Daphnia (1 day old) and Guppy (3 weeks old) in order to estimate EC_{50}-values. The results are summarized in table III.

The EC_{50} of α-HCH on Chlorella, based on growth effect, was higher than the solubility in water (10 ppm).

Daphniae and guppy's showed paralysis after exposure to α-HCH. This criterion, combined with mortality, was chosen as response for the determination of an EC_{50}-value.

For daphniae the reproduction proved to be a still more sensitive criterion: from fig. 5 it can be derived that the EC_{50} on reproduction is

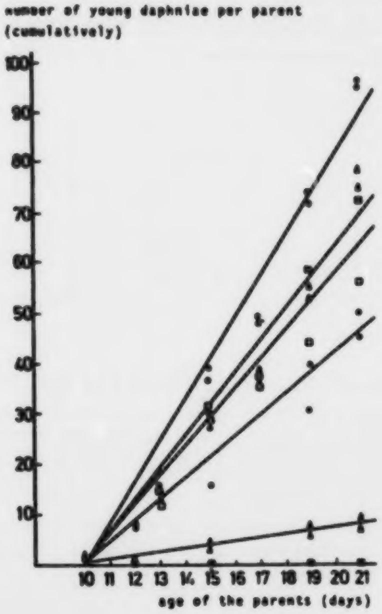

Fig. 5 Reproductive capacity of Daphnia magna as a function of the α-HCH concentration in the medium

○ blank
△ 0.01 ppm α-HCH
□ 0.05 " "
● 0.20 ppm -HCH
▲ 1.00 " "
■ 2.00 " "

about 0.10 ppm (therefore the 0.80 ppm dosage level was not applied in the studies mentioned in section I (4) and (5), as under these circumstances not enough young daphniae could be obtained for the analysis of α-HCH).

From the EC_{50}-value on the reproduction of daphniae (or better the EC_{10}-value, which can be obtained by graphic extrapolation) a tentative ecological limit for α-HCH can be derived by applying two safety-factors of 10 (one for extrapolation to the total ecosystem, to other criteria and to other organisms; one for possible synergistic effects between α-HCH and other chemicals), in analogy to the approach common in food-toxicology.

Applied to an EC_{10}-value of 0.005 ppm for the reproduction of daphniae this approach yields a tentative ecological limit of 0.05 ppb for α-HCH. This value clearly is lower than the "normal" content of α-HCH in e.g. the Rhine river (0.1 - 0.5 ppb).

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DISCUSSION

PRINZ (Federal Republic of Germany)

Did you make any attempts to develop a mathematical model to your experimental investigations about accumulation and elimination of αHCH?

CANTON (Netherlands)

We didn't make any attempts in that direction as yet.

MEASURES OF ASSOCIATION OF SOME AIR POLLUTANTS, NATURAL IONIZING RADIATION AND CIGARETTE SMOKING WITH MORTALITY RATES

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ABSTRACT

Two methods are employed to estimate the association of hydrocarbons, sulfur compounds, nitrogen compounds, natural ionizing radiation, and cigarette smoking with some age stratified and disease specific United States mortality rates for white males. The first method is based on a ridge regression technique and the second on a sign constrained least squares analysis. The measure of association between these environmental factors and mortality are quantified as elasticities; i.e., the indicated percentage change in the average mortality rate corresponding to a 1% change in the average level of the environmental factor. Elasticities are estimated for age specific and disease specific mortality rates, and these values are then aggregated and compared to estimates corresponding to total mortality rates. Overall, consistent results are obtained using the above methods for sulfur compounds and cigarette smoking. Many of these results differ considerably from corresponding results obtained from the ordinary least squares regression analysis, highlighting the need for applying the appropriate estimation methods. In addition to the variables already specified, these analyses take into consideration the following groups of explanatory variables:

Climate - *Precipitation, January temperature, July temperature, humidity, and solar radiation.*

Socioeconomic - *Age, education, sound housing, population per household, population density, % non-white, % white-collar, income, and city size.*

1. INTRODUCTION

Multiple regression analyses on large data banks of mortality rates and pollution measures have indicated an association between environmental pollution levels and increased mortality. Lave and Seskin, Hickey, et al. and Carnow and Meier are among several authors who have recently studied the chronic health effects of pollution by means of multivariate regression analysis including as explanatory variables a number of interdependent urban factors which affect health. Neyman has illustrated pitfalls in multipollutant, multilocality studies. Specifically, he pinpoints the problem of incomplete comprehensiveness of the set of pollutants studied and the subsequent results in the following statement: "if the study involves a certain numbers of pollutants, say $P_1.P_2,\ldots,P_s$, but neglects another pollutant P_0 that happens to be important, the conclusions regarding $P_1,P_2,\ldots,P_s$, suggested by even very highly significant findings, may be completely misleading."

To address this criticism of previous studies, we have included in this study a rather broad (but still incomplete) list of explanatory variables. Both gaseous and particulate forms of pollutants from both mobile and stationary sources are included in this study along with natural ionizing radiation, smoking, four climate and ten socioeconomic variables.

Rienke has pointed out that in many studies where data is not obtained from a well designed or controlled experiment, as is the case in air pollution studies involving socioeconomic, climate and other uncontrolled variables, nonorthogonality requires that estimation of individual effects be handled by techniques other than ordinary least squares. He suggested that ridge regression, as first described by Hoerl, provides a promising method for avoiding distortion due to nonorthogonality. Recently, McDonald and Schwing have provided an example illustrating the differences between ridge regression estimates and least squares regression estimates of the coefficients in a model relating air pollution to a total mortality rate.

This paper is primarily concerned with point estimates of the association of several indices of mortality with pollution based on a multiple linear regression model containing 23 explanatory variables. A description of the variables is contained in the next section. Least squares, ridge regression and sign constrained methodologies are described in Section 3. One of four results sections, (4.4, Aggregation of Associations) is presented here. Section 4.1, Disease Specific Results; Section 4.2, Age Specific Results; and Section 4.3, Age Specific Results for the Lung Cancer and Arteriosclerotic Heart Disease Category are not presented here due to lack of space.

It is appropriate to emphasize that any regression model has numerous limitations. A linear model, as used in this study, can be considered as only an approximation to a more complicated underlying model. This approximation has greatest validity in the neighborhood of the point where each variable assumes its mean value. Further, in any epidemiological study such as this, the explanatory variables cannot be controlled and thus may be associated in unknown ways with other hidden but influential variables. Averaged explanatory variables and aggregated response variables do not completely define the exposure patterns and mortality patterns of the large populations in our study communities. Migration habits, diagnostic biases, exposure histories, synergisms and personal and dietary habits have not been quantified and therefore are not usually included in global studies of this type. Most important, correlations or associations between environmental factors and health effects do not prove causation. One can only infer the degree of association. Nevertheless, the model is frequently used as a tool in quantifying the association of certain environmental factors with health indices such as mortality rates.

2. DESCRIPTION OF VARIABLES CONSIDERED

To refine our estimates of the associations of certain environmental factors with health, three groups of mortality data for the years 1959-1961 from Duffy and Carroll are studied as dependent variables. Briefly, they are:

1. The highest fifteen specific white male disease categories which make up the bulk (65%) of the total white male mortality rate.
2. Total white male and age stratified white male mortality rates.
3. Age stratified white male mortality rates due to arteriosclerotic heart and coronary and age stratified mortality due to lung cancer, the largest and third largest white male disease categories, respectively.

Preference is given to using the white male category of the mortality rates since these rates are usually based on large populations with a large number of deaths, and are thought to represent a wide exposure to the various environmental conditions.

A total of 23 explanatory or "independent" variables are used in this study.These socioeconomic, climate, pollution, cigarette smoking, and natural ionizing radiation variables are described in the complete text of this paper. Summary statistics of the explanatory variables are also presented for the 46 Standard Metropolitan Statistical Areas (SMSA's) in this sample. Many of the explanatory variables tend to be highly correlated. The degree of correlation is particularly high among pollution variables, in part because prevailing weather factors often determine whether or not pollutants emitted into a community accumulate or disperse. For example, the correlation coefficient between some pollutants is as high as 0.877.

It is believed that the associations are affected not only by the long-time average concentration of a pollutant but also by its physical and chemical form as well as by its pattern of short-time variation. Consequently, to investigate the possible effects of such pattern variation, the mean and minimum of some of the pollutants are included as separate variables in the regression analyses. Difficulties in fitting the linear model which arise as a result of high correlations and possible redundancies among explanatory variables are diminished by the use of ridge regression and sign constrained least squares regression.

Though the methodologies employed are intended to diminish the difficulties encountered when collinear variables are included, some difficulties or uncertainties in interpretation remain due to the fact that certain variables serve as surrogates for variables not included separately. For example, the hydrocarbon emissions from automobiles are so closely linked to carbon monoxide and tetraethyl lead that the hydrocarbon pollution potential can be considered a surrogate for these compounds as well. The natural ionizing radiation index is related to altitude, a possible factor in mortality. Finally, the smoking index is possibly correlated with other stress related habits including alcohol and coffee consumption.

3. METHODOLOGY

Multiple linear regression techniques have played a prominent role in studies of the association between air pollution and mortality (and/or morbidity) rates. The mathematical model used in these analyses is the multiple linear regression model, $y = x\beta + \epsilon$. The quantity y is the vector of n observations on the dependent variable, x is the (n by p) matrix of p explanatory variables for the n observations, β is the vector of unknown regression coefficients, and ϵ is the vector of errors. The error terms are assumed to be uncorrelated with a mean equal to zero and common (unknown) variance. The variables are assumed to be transformed so the x'x is in the form of a correlation matrix, where x' denotes the transpose of the matrix x. Having specified this linear form as a basic model, three methods of estimating the standardized regression coefficients will be considered: the least squares method, a ridge regression method, and a sign constrained least squares method.

Ridge regression, the second method applied in this paper, is an estimation procedure based upon $\hat{\underset{\sim}{\beta}}(k) = (x'x + kI_p)^{-1}x'y$, $k \geq 0$, and as such defines a class of estimators where k is a scalar index and I_p is the (p by p) identity matrix. Note that $\hat{\underset{\sim}{\beta}}(0)$ is the usual least squares estimator denoted simply by $\hat{\underset{\sim}{\beta}}$. The ridge estimator minimizes the residual sum of squares subject to a constraint on the length of the estimator, $\sqrt{\hat{\underset{\sim}{\beta}}'(k)\hat{\underset{\sim}{\beta}}(k)}$. In fact, the length of $\hat{\underset{\sim}{\beta}}(k)$ is a decreasing function of k. For $k > 0$, the estimator $\hat{\underset{\sim}{\beta}}(k)$ is biased; however, the total variance, i.e., the sum of the variances of the individual coefficients, decreases as k increases.

As a third method of arriving at point estimates of regression coefficients, the residual sum of squares was minimized subject to inequality constraints on the seven explanatory pollutant variables: hydrocarbon potential, sulfur dioxide potential, NO_2, minimum sulfate, mean sulfate, minimum nitrate and mean nitrate. These coefficient estimates were constrained to be non-negative. In all cases, the unconstrained least squares solution violated one or more of the constraints. Since the restricted solution must then lie on at least one of the violated boundaries, the data was fit subject to all $(2)^7$ possible combinations of variable delations.

4. RESULTS - POLLUTANTS, RADIATION AND SMOKING

The results from this study for nine of the explanatory variables are given in three groups of white male mortality rates: the fifteen high disease categories; the age stratified total mortality rates; and the age stratified lung cancer rates and age stratified arteriosclerotic heart and coronary rates. The nine explanatory variables of concern here are the seven pollution variables, the natural ionizing radiation variable, and the smoking index variable. The "measure" of association presented in this study is an elasticity, i.e., the estimated percent change (either increase or decrease) in the average mortality rate of the given disease (and/or age) category corresponding to a one percent increase in the average of the given explanatory variable, holding all other variables fixed at their average values. The elasticity of a given mortality rate and explanatory variable is obtained using the regression coefficient estimates.

4.1 Fifteen high Disease Categories for White Males - presented in complete text.

4.2 Age Stratified White Male Mortality Rates - presented in complete text.

4.3 Age Stratified White Male Lung Cancer Rates and Age Stratified White Male Arteriosclerotic Heart and Coronary Rates - presented in complete text.

4.4 Aggregation of Associations - To assess the relative magnitude of the associations of the explanatory variables. The associations of three sulfur pollutants, SO_2, minimum sulfate, and mean sulfate, are grouped together as are the associations of three nitrogen pollutants, measured NO_2, minimum nitrate, and mean nitrate.

Similarly, the age specific elasticities are multiplied by the age specific rate and by the fraction of white males in the specific white male age group. These appropriately weighted elasticities are aggregated over the ten age groups and over like pollutants to assess the net change in total white male mortality associated with a 1% change in specific variables or groups of variables.

Three different data sets have been used to estimate the associations of explanatory variables, individually or as groups, with white male mortality: (1) the sum of the effects on the 15 most prominent disease categories (assuming pollutant association with mortality is confined to the fifteen disease categories), (2) the sum of the effects on each of the 10 age categories and (3) the total mortality data. The three data sets indicate that a 1% decrease in the sum of sulfur compounds is associated with decreases in average white male mortality rates of .028, .022 and .025% respectively using the ridge method, and .045, .034 and .031% respectively using the sign constrained method. The sign constrained estimate was consistently higher in each set b, approximately 60%. These data also indicate that a 1% decrease in the nitrogen pollutants studied is associated with decreases in average white male mortality rates of .020, .009 and .007% respectively using the sign constrained method while the ridge method provides associations of opposite sign with values -.005, -.007 and -.006%. In these analyses two positive associations are indicated on mortality with the hydrocarbon variable. All other estimates of the association are either negative or zero. The fact that sulfur compounds consistently show associations greater than nitrogen compounds is consistent with another study which compares these compounds.

The estimates resulting from a 1% change in ionizing radiation are highly irregular. An increase in mortality as large as .014% is associated with radiation using the age summation and sign constrained estimate while a decrease in mortality of .044% is associated with radiation using the disease summation and ridge estimate. Recall that in the sign constrained method, only the pollutant coefficients are constrained; radiation and cigarette smoking are not constrained.

Using the same three data sets, a 1% decrease in cigarette smoking corresponds to decreases in white male mortality rates of .081, .092 and .096% with the ridge method and .069, .106 and .11% using the sign constrained method. A decrease in the mortality rates corresponding to an increase in cigarette smoking is indicated for some disease categories. These negative quantities are as yet inadequately understood and deserve further investigation. Although they might be the result of a "beneficial" effect of smoking, it seems more likely they would be, in part, the result of a reallocation of deaths among the various disease categories (e.g., increased mortality from arteriosclerotic heart at an early age reducing the possibility of death from cerebral hemorrhage later). There are, of course, other possible explanations. For example, the linear, additive model may not be entirely appropriate and/or the data base may be deficient in some not yet specifically identified ways.

Aggregates from the age stratified white male lung cancer and age stratified white male arteriosclerotic heart mortality rates were calculated. As in the total mortality comparisons, the various estimates of the association of mortality with the sulfur pollutant group are all positive. In the lung cancer category they are .016, .041, .017 and .019%. In the arteriosclerotic heart disease category they are .025, .026, .027 and .005%. Sign discrepancies again exist for the associations of mortality with nitrogen compounds. The values are -.007, .017, .001 and .000% in the lung cancer category and -.035, .000, -.038 and .000% the arteriosclerotic heart disease category. Generally the associations obtained for the hydrocarbon pollutant are close to zero, while the corresponding values for the radiation variables are uniformly negative. The values for the association of these diseases with cigarette smoking are within very narrow bands. For lung cancer the associations are .278, .289, .279, and.302% for a 1% change in the smoking variable and for arteriosclerotic heart disease they are .180, .193, .208 and .228% for a 1%

change in the variable.

5. CONCLUSIONS

In order to somewhat substantiate estimates of association, many checks should be made within a given analysis. For example, the internal consistency of the data itself needs to be examined. The sensitivity of the parameter estimates needs to be investigated as either the objective function (in this study, the residual sum of squares) and/or method of estimation is modified. In this study, consistency of the data and corresponding estimates is considered by examining disease and age stratified mortality rates, and then comparing corresponding aggregated results with the appropriate total mortality results. The sensitivity of parameter estimates has been examined by considering two methods of biased estimates - namely, a ridge regression technique and a sign constrained least squares method.

As noted, there is excellent agreement among the estimates of the cigarette smoking index elasticity. The six estimates range from .069 to .110. Likewise the six estimates of the elasticity for sulfur compounds also fall within a relatively narrow range .022 to .045. Nitrogen compound elasticities (-.007 to .020) vary substantially in magnitude and sign, leaving great uncertainty for this group. In these 40 regressions, one disease specific rate, endocarditis and myocardial degeneration, provides a substantial association of the hydrocarbon index with mortality. A comparable association is not found in the age stratified or total mortality estimates.

Based on the data used in this study, we conclude that: (1) increased concentration of sulfur compounds are associated with a general increase in the total white male mortality rate, (ii) increased consumption of cigarettes are also associated with increases in the total white male mortality rate, and (iii) associations for nitrogen compounds, the hydrocarbon index, and ionizing radiation are dependent on methodology and data stratification.

A complete report of this study (including a thorough description of variables, summary statistics, illustrations, description of results, and a bibliography) is available from the authors.

DISCUSSION

JACOBSEN (U.K.)

1. What was the correlation coefficient between the variables NO_x and HC illustrated in your slide?

2. Would you agree that there is a general philosophical difficulty in the use of the "ridge" repression method (apart from the problem of biased estimation)?

It seems to me that "ridge" regression is an attempt to "orthogonalise" data that are inherently non-orthogonal. How can one expect to extract information from a data-matrix which, by definition, does not contain the required information?

SCHWING (U.S.A.)

1. The illustration was taken from our earlier publication on ridge analysis. I'm sure the correlation coefficient in that study was greater that 0.9 and therefore, we see a dramatic effect. In the data reported on today, the correlation coefficients were substantially lower, of the order of 0.8. The effects, though less dramatic, still exist.

2. The objective in applying ridge regression is not to extract information which does not exist. The objective is to illustrate and avoid pitfalls in the interpretation of least squares coefficient estimates obtained from nonorthogonal data.

STEPANEK (CSSR)

Was the model chosen with regard to the large number of controlled variables or was the linearity of the model tested at least with respect to some of the controlled variables?

SCHWING (U.S.A.)

Our 23 explanatory variables were not controlled in this study. Although our previous study considered linear and log functions of some uncontrolled variables, the results reported today were obtained with a linear model only.

BODY BURDEN OF POLLUTANTS: COMPARTMENTAL STOCHASTIC MODELS

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University of Maryland, Baltimore County, Baltimore, Md, USA

ABSTRACT

The transport of trace pollutants and radioactive tracers through the body is usually modeled as a multicompartment linear differential system with constant exchange rates. Specific activity curves in constant exchange rates. Specific activity curves in constant environments must then necessarily be mixtures of exponential functions of time. Environmental health standards can thus be set in terms of averaging times appropriate to the time-scale for exponential decrease ("biological half-life"). Two serious defects in this concept are exhibited. First, when uptake rate depends on the remaining uncontaminated volume in a compartment, the half-life for uptake decreases with increasing concentration so that brief exposures to high concentrations may do less harm than predicted by the usual compartmental model. This is illustrated by the elimination and uptake of carbon monoxide in rats and humans. A second difficulty is that specific activity curves (here interpreted as the probability density for time of transport of pollutant) are often power functions of time rather than exponential functions, especially for bone-seeking elements. The linear compartmental model is inadequate and an alternative model, with transitions governed by a Markov process and times between transitions determined by a random walk process, appears to be needed.

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1. Introduction

A very difficult problem in establishing safe dose levels for environmental pollutants is that the concentration of a pollutant to which an individual is exposed may fluctuate significantly over times comparable to, or much shorter than, the characteristic lifetime of the pollutant in the organ of interest. The ability of an organ (or perhaps the whole body) to excrete a contaminant in due course must be explicitly taken into account in order to estimate the maximal safe dose. This is usually done by establishing safe levels based on appropriate averaging times. For example, the maximal allowable concentration of carbon monoxide (CO) in the U.S. is 35 ppm for a one-hour average, and 9 ppm for an 8 hour averaging time. The averaging time concept leads to mathematical and practical difficulties in assessing fluctuating concentrations [1] [2] [3] [4]. If fluctuations in pollutant concentration occur much more rapidly than the biological half-life of a critical organ, it is claimed that the organ will not respond much to these fluctuations - that is, a brief exposure to a very high concentration will not cause much harm. However, this conclusion depends on a linear model of physiological kinetics which has several serious defects, as we shall presently demonstrate. That is, even though brief high exposures do not violate long averaging time standards, they may do much less damage than expected.

2. Compartmental Models

We assume that the body can be divided into n subsystems or compartments, depending on the pollutant. For carboxyhemoglobin (COHb) in the blood due to CO exposure, we could use n=1 (arterial blood) or n=2 (say lungs, blood; alternatively [5] blood in which CO is bound to Hgb, and muscle or liver in which CO is bound to other hemeproteins). For lead and other boneseekers, we may need n=3 [6]: (mainly) blood, (mainly) soft tissue, and (mainly) skeleton. The basic compartmental model is developed by many authors (see [7] for references). Let $X_j(t)$ be the amount of pollutant in compartment j at time t. Let V_j, a constant, be the maximum volume in compartment j. Let A_j be the endogeneous production rate of pollutant in compartment j. Let $C_j(t)$ be the external concentration to which j is exposed at time t. We may thus incorporate the effects of different pathways to different organs e.g. lead exposure by both breathing and eating lead. Let X, A, C be the corresponding n-vectors, say X', $X' = (X_1, \ldots, X_n)$. Let K, L be $n \times n$ matrices, and let LC be an $n \times n$

diagonal matrix in which the diagonal term $L_{ii}C_i$ is the uptake rate per unit volume in organ i when exposed to C_i. It is usually postulated that

$$dx/dt = A + LCV - KX \tag{1}$$

$$= B - KX \tag{2}$$

where

$$B = A + LCV \tag{3}$$

the general solution is

$$X(t) = \exp(-Kt)X(0) + \int_0^t \exp(-K(t-u))B\ du \tag{4}$$

allowing $B = B(u)$ to also depend on time if (as is the case in a real environment) $C(t)$ depends on time t. In the usual clinical situation of exposure to a constant environment, we have in general for constants F_{ij}, G_j

$$X_i(t) = \sum_{j=1}^{n} F_{ij} \exp(-G_j t) + X_i(\infty) \tag{5}$$

where G_j is an eigenvalue of K (assumed all distinct herein). When $n=1$, this is the usual "half-life" phenomenon.

In reality, the uptake rate depends on the remaining volume in compartment j, which is $V_j - X_j$, so that instead of equation (1) we ought to write

$$dX/dt = A + LC(V-X) - KX \tag{6}$$

$$= B - MX$$

where B is the same as (3) and

$$M = LC + K \tag{7}$$

hence

$$X(t) = \exp(-T(t))X(0) + \int_0^t \exp(T(u) - T(t))B(u)\ du \tag{8}$$

The random time T is defined by

$$T(t) = \int_0^t M(u)\ du \tag{9}$$

The basic representation is different. In (4), $X(t)$ is a linear filter of the concentration C; in (8), $X(t)$ is not a linear filter of C since the exponential elimination rate depends also on the previous exposure history.

This difference is not important when C_j is very small; it is important in some practical situation such as the elimination and uptake of carbon monoxide. Applying (8) for a one-compartment ($n=1$) model for COHb in rats and in humans, I found [8] that (8) gives an excellent description of the data, including the highly consistent observation that the timescale for elimination ($C=0$) namely $1/K_{11}$, is always longer than the timescale for uptake as a result of exposure to C ppm CO, namely $1/M_{11} = 1/(K_{11} + L_{11}C)$. This exhibits a larger assimilative capacity than predicted by (4) since pollutants are eliminated more rapidly at higher concentrations than at lower concentrations. (See Sec. 4 for some examples.)

3. Power Laws

A second and most serious difficulty is that much data on radioactive tracers and trace contaminants is not at all like (5) but is much better described in practice by a power law

$$Xn(t) = F_n t^{-\alpha-1} \tag{10}$$

Bone-seeking elements - calcium, lead, strontium are of special environmental significance - exhibit this power-law behavior [9] [10] [11]. A number of models have been proposed to explain the observed power-law behavior [12] [13] [14]. I have developed [15] a flexible 4-parameter random walk model which, upon adjustment of various combinations of parameters, can fit all of the proposed distributions for the time of passage of a molecule through a compartment - gamma, power-law (skew stable) and exponentially modified skew-stable. To relate these to various compartments requires a fundamentally different orientation, in which the allocation of molecules to various compartments is modeled a Markovian transition process, and the residence time between transitions can have any distribution. This formalism is known as a Markov renewal process; its consequences will be developed elsewhere. It is sufficient to note here that no variant of the usual compartmental model (1) yields power-law behavior like (10). A safe dose-exposure relation cannot therefore be built on the averaging-time concept.

The new formulation of the problem is that the specific activity in the ultimately observed compartment n, say $X_n(t)$, will be taken as the first passage time probability density function if a molecule of pollutant is immediately excreted from compartment. If molecules recirculate indefinitely without being excreted, then $X_n(t)$ may be taken as the renewal density (i.e. recurrence density) function for compartment n. We will now consider only excretable molecules. The Markov renewal postulates are:

(a) Transitions of a molecule from compartment i to compartment j occur independently of each other, with no memory of earlier transitions -- i.e., as a Markov process with transition probability matrix $P = ((P_{ij}))$.

(b) The passage time from i to j, say T_{ij}, is a random variable whose distribution depends on i and j, but is independent of anthing else.

It is conceptually easy -- but difficult in practice -- to derive the distribution of the first passage time to compartment n given P and the distribution of the T_{ij}. In general, there is no way to obtain power law behavior without having a power law transition distribution for some essential precursor transition time T_{ij}. This can be obtained readily for the bone-seeking elements, using the concept of a continuously expanding calcium pool developed by BURKINSHAW et. al. [12]; see [15] for details. The main idea in 15 is that the exchangeable calcium pool -- the total number of calcium molecules available for subsequent transition or elimination -- is increasing essentially linearly with time. This will automatically decrease the proportion of contaminant available for transition, but at a much slower rate than the essentially exponential decrease required by the constant exchange rate model expressed by (1). This can be readily extended to derive power law transition distributions for random numbers of transitions as well as single-step transitions.

4. Example: One-compartment Model for Carbon Monoxide

In [8] I used data by PETERSON et. al. [16] and MONTGOMERY et. al. [17] to determine parameters for the one-compartment (n = 1) model (8) with constant exposures at C ppm CO. $X_1(t)$ was the observed concentration of carboxyhemoglobin in the blood of the subject.

TABLE I

Parameters for the uptake and elimination of CO by rats

C (ppm)	K_{11} (min^{-1})	M_{11} (min^{-1})	$X_1(\infty)$	B_{11}/C (min^{-1})
150	0.02241	0.02105	0.1622	$2.27\ 10^{-5}$
250	0.02046	0.02294	0.2368	$2.17\ 10^{-5}$
500	0.01968	0.02674	0.4351	$2.37\ 10^{-5}$
1000	0.01964	0.04167	0.6305	$2.63\ 10^{-5}$

TABLE II

Parameters for the uptake and elimination of CO by humans

Subject	K_{11} (min^{-1})	M_{11} (min^{-1})	$X_1(\infty)$	B_{11} (min^{-1})
1	0.002624	0.002820	0.07756	$2.19\ 10^{-4}$
2	0.002737	0.002833	0.08114	$2.30\ 10^{-4}$
3	0.002386	0.002699	0.08556	$2.31\ 10^{-4}$

(The subjects were inactive young men exposed to 50 ppm CO.)

The model not only proved self-consistent, it also provided an excellent fit to the data. Note that in general, M_{11} is larger than K_{11}.

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ANALISI DI REGRESSIONE DEI VALORI DI PIOMBO NEL SANGUE SULL'ESPOSIZIONE ATMOSFERICA

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RIASSUNTO

In questo lavoro è discussa una funzione modello iperbolica in alternativa a quelle già proposte per l'analisi di regressione dei valori di piombo nel sangue sull'esposizione atmosferica, nel tentativo di migliorare l'interpolazione con un modello più rispondente alla realtà fisica della relazione dose-risposta. Come esempio è considerata l'applicazione a dati della letteratura.

ABSTRACT

This paper discusses a hyperbolic model function as an alternative to those already proposed for regression analysis of lead levels in blood as a function of atmospheric exposure. The aim is to achieve improved interpolation with a model corresponding more closely to the physical reality of the dose-response relationship. Data taken from the literature are used in sample applications.

1. Introduzione

Da qualche tempo sono disponibili dati medi di concentrazione di piombo nel sangue, rilevati in campioni provenienti da aree urbane, assieme alla stima dell'esposizione atmosferica al piombo particellare proveniente dai gas di scarico degli autoveicoli (The Working Group on Lead Contamination [1]). Con l'assunzione che i campioni appartengano ad una popolazione avente un apporto costante nella dieta, i dati sono stati interpolati con una funzione esponenziale (Goldsmith e Hexter [2]). Altri dati si riferiscono a valori di esposizione notevolmente più precisi dei precedenti, perchè ricavati da esperienze di laboratorio, nelle quali viene simulato e controllato nel tempo l'evento inquinante (Knelson, Johnson, Coulston, Golberg e Griffin [3], Cole e Lynam [4]). Il modello logaritmico si adatta a descrivere la concentrazione di piombo nel sangue in funzione del tempo di esposizione, quando quest'ultima viene mantenuta ad un valore costante (Knelson *et al*, [3]). Recentemente è stata proposta la funzione iperbolica quale curva interpolante (Favretto Gabrielli [5]). Tale funzione contiene un parametro di saturazione, in accordo con il raggiungimento di una concentrazione costante di piombo nel sangue dopo un tempo prolungato di esposizione (Cole e Lynam [4]).

In questa ricerca vengono confrontati i modelli già proposti con il modello iperbolico, riportando come esempio la discussione dei dati di Goldsmith e Hexter [2] e di Knelson *et al*. [3].

2. Analisi di regressione

L'analisi di regressione è stata effettuata utilizzando un programma di minimi quadrati per la stima dei parametri non lineari (Marquardt, Baumeister, Sheldon e Stanley [6]) su un calcolatore CDC 6200 del Centro di Calcolo dell'Università di Trieste. Come indice di adattamento dei dati alla funzione modello è stato considerato lo scarto quadratico medio dei valori osservati da quelli calcolati.

3. Risultati e discussione

La tabella I riporta i valori dei parametri calcolati mediante regressione non lineare dai dati di Goldsmith e Hexter [2] con vari modelli. La figura 1 riporta come esempio l'andamento della curva calcolata assumendo il modello iperbolico. Tale modello, scritto in forma di equazione "tipo Langmuir", è stato già utilizzato per descrivere l'assorbimento di piombo da parte del tessuto osseo (Mac Donald, Nusbaum, Ezmirlian, Barbera, Spain e Rounds [7], Gitelman e Neumann [8]).

TABELLA I

Esempio di regressione non lineare dei valori di piombo nel sangue (y, μg Pb/100 ml di sangue) sui dati di esposizione atmosferica (x, μg/m³ di aria). 30 coppie di osservazioni tratte da Goldsmith e Hexter [2]. s, scarto quadratico medio.

Funzione modello	Parametri a	b	c	s
$y = ax^b$ *	18.1	0.239	-	± 3.0
$y = a + b \log_{10} x$	17.8	13.9	-	± 3.5
$y = c + \frac{abx}{1 + ax}$	0.0883	35.1	15.7	± 3.1

* *Proposta da Goldsmith e Hexter nella forma linearizzata:*

$$\log_{10} y = \log_{10} a + b \log_{10} x$$

La funzione iperbolica a tre parametri descrive l'andamento dei punti nella stessa misura di quella esponenziale, come appare dal confronto dei valori di s, mentre con la funzione logaritmica l'adattamento è minore. Inoltre nella funzione iperbolica l'intercetta c = 15.7 μg Pb/100 ml di sangue, stabilisce l'apporto della dieta e di altre fonti, che determinano il livello base di piombo nel sangue. Kehoe [9] e Azar, Snee e Habibi [10] sostengono che l'influenza del piombo atmosferico sul tenore di piombo nel sangue risulta inferiore a quella supposta in base alla relazione di Goldsmith e Hexter: il modello da noi proposto consente di interpretare i dati differenziando il con-

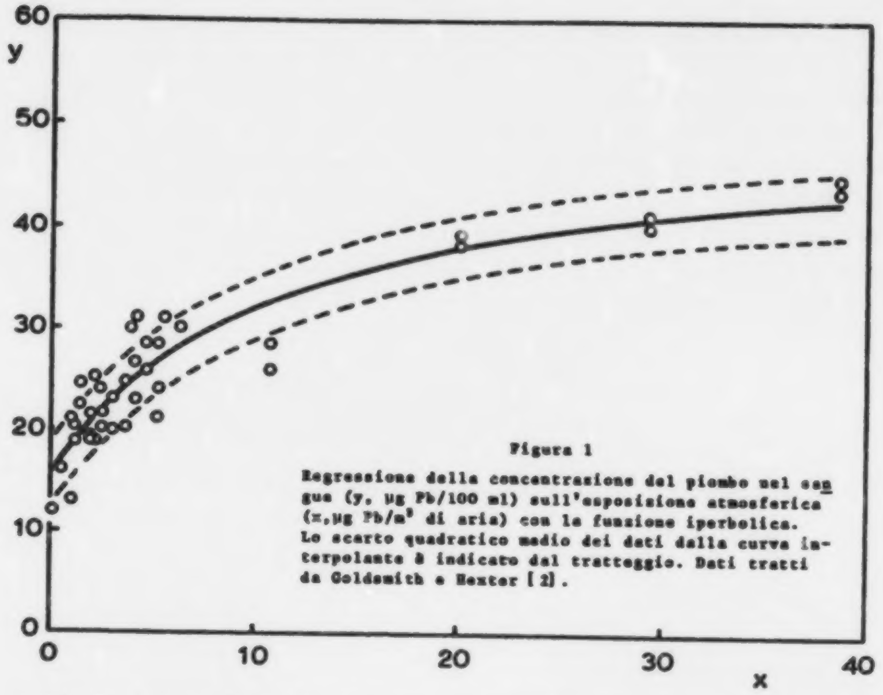

Figura 1

Regressione della concentrazione del piombo nel sangue (y, µg Pb/100 ml) sull'esposizione atmosferica (x, µg Pb/m^3 di aria) con la funzione iperbolica. Lo scarto quadratico medio dei dati dalla curva interpolante è indicato dal tratteggio. Dati tratti da Goldsmith e Hexter [2].

tributo della dieta (supposto costante) dall'esposizione atmosferica. A basse esposizioni ($x \to 0$) y tende all'espressione $y = c + abx$, cioè la concentrazione di piombo nel sangue varia quasi linearmente con l'esposizione, in accordo con le osservazioni di Goldsmith [11]. Un'ultima caratteristica del modello è il parametro di saturazione (b). In teoria un limite di saturazione potrebbe rappresentare il piombo nel sangue in equilibrio sia con quello presente in altri tessuti di deposito, che con una certa esposizione media. Il modello fisico giustifica il livello di saturazione, dato che tale livello si ritrova nell'esposizione prolungata ad una concentrazione costante di polluente.

Le osservazioni di Knelson *et al.* [3] possono essere utilizzate per tale controllo: i dati hanno il pregio della precisione nella variabile indipendente (tempo), precisione che rappresenta uno dei requisiti per una corretta applicazione dell'analisi di regressione; viceversa nei dati raccolti da Goldsmith e Hexter, eterogeneità campionaria ed imprecisione nella stima di x a basse esposizioni ($x < 5$ μg Pb/m^3 di aria, dove diventano notevoli gli errori derivati per la pendenza della relazione $y = y(x)$) contribuiscono sensibilmente alla dispersione dei dati.

Knelson pone in relazione l'aumento potenziale del piombo totale nel sangue (4.9 litri) con l'aumento del carico totale di piombo nell'organismo, quest'ultimo ricavato dalla concentrazione di piombo nell'aria respirata, tenendo conto di costanti quali la ventilazione polmonare, la frazione di piombo inalato. Esperienze in parallelo controllano continuamente l'apporto di piombo non atmosferico.

I risultati dell'analisi di regressione dei dati di Knelson *et al.* [3], appaiono nella tabella II. La figura 2 riporta l'interpolazione con la funzione iperbolica. Quest'ultima rappresenta anche in questo caso un modello valido. Dal valore del parametro di saturazione si può ricavare il limite teorico di concentrazione di piombo nel sangue ad un'esposizione continua. Per le due esposizioni sperimentate si ottengono così i seguenti valori limite:

Esposizione continua (μg Pb/m^3 di aria)	Concentrazione limite (μg Pb/100 ml di sangue)
3.2	7.9
10.9	23.9

Da rilevare che, qualora alla concentrazione limite si aggiunga il livello di base, il primo punto (7.9 + 15.7 = 23.6) giace sull'iperbole interpolante i valori di Goldsmith e Hexter (per $x = 3.2$, $y = 23.3$), mentre il secondo (23.9 + 15.7 =

TABELLA II

Analisi di regressione non lineare (su N dati) dell'aumento del contenuto di piombo nel sangue (y, mg in 4.9 litri di sangue) sull'aumento del carico totale di piombo nell'organismo (x, mg) a due esposizioni. Dati tratti da Knelson et al. [3]. *s, scarto quadratico medio.*

Funzione modello	Esposizione: 3.2 µg/m³, N = 10			Esposizione: 10.9 µg/m³, N = 16		
	a	b	s	a	b	s
$y = a + b \log_{10} x$ *	0.205	0.182	± 0.038	0.326	0.556	± 0.070
$y = \frac{abx}{1 + ax}$	1.09	0.387	± 0.034	0.336	1.17	± 0.067

* *Proposta da Knelson et al.* [3].

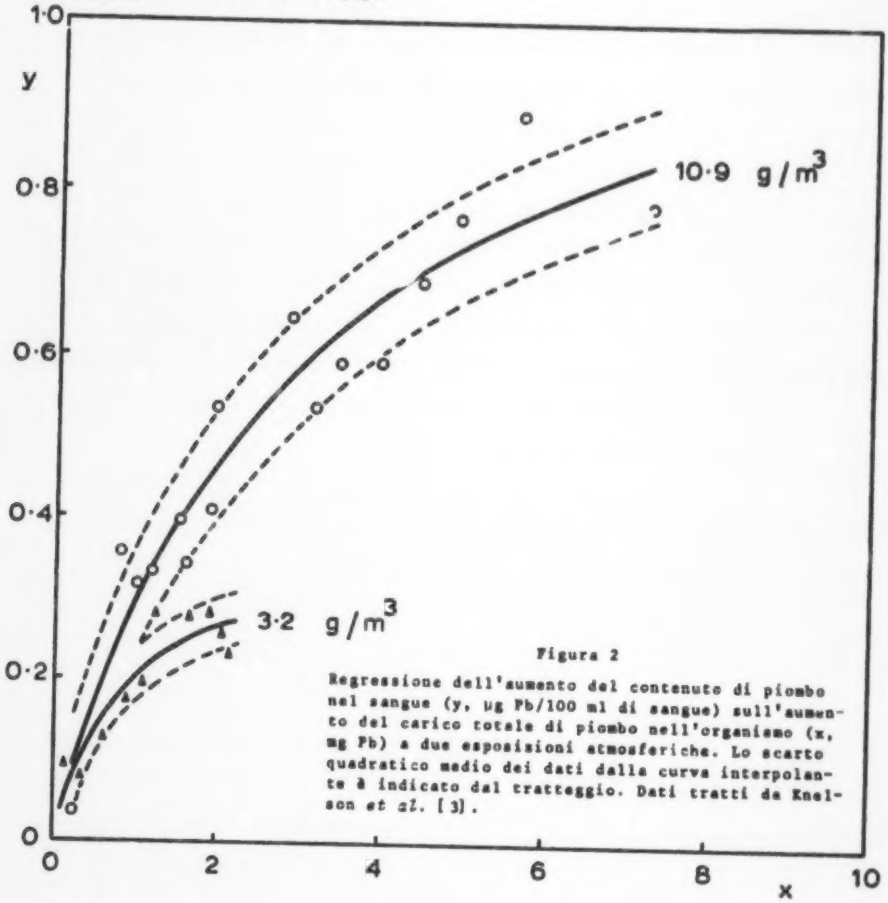

Figura 2

Regressione dell'aumento del contenuto di piombo nel sangue (y, µg Pb/100 ml di sangue) sull'aumento del carico totale di piombo nell'organismo (x, mg Pb) a due esposizioni atmosferiche. Lo scarto quadratico medio dei dati dalla curva interpolante è indicato dal tratteggio. Dati tratti da Knelson *et al.* [3].

= 39.6) risulta circa 20% maggiore del valore sull'iperbole (per x = 10.9, y = 32.8).

4. Conclusioni

La presente ricerca vuol essere soltanto un suggerimento tendente a sottolineare l'utilità del modello iperbolico nell'analisi di regressione della concentrazione di piombo nel sangue sull'esposizione atmosferica. Ulteriori esperienze di esposizione continua, anche a livelli più elevati, potrebbero consentire di stabilire con maggior precisione l'andamento della relazione empirica piombo nel sangue-esposizione atmosferica continua, che non la raccolta di dati in popolazioni urbane, dove sorgenti di variazione incontrollabili oscurano l'andamento stesso.

Ricerca eseguita con il contributo del Consiglio Nazionale delle Ricerche

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SUR UN MODELE EPIDEMIOLOGIQUE, STOCHASTIQUE ET COMPARTIMENTAL SIMULANT L'APPARITION ET L'AGGRAVATION DE LA SURDITE

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RESUME

Les résultats d'enquête audométriques-sonométriques, dont on dispose à l'heure actuelle, sont hétérogènes. En effet, le seuil de déficit auditif à partir duquel la surdité est présumée, varie: 25dB dans la Recommandation ISO R/1999 et 35dB dans le tableau français des Maladies Professionnelles, par exemple. Le déficit moyen pratique lui-même donne suivant le cas plus ou moins d'importance à la fréquence conversationnelle 1000 Hz. Il en résulte que la fréquence F(t,b) des surdités professionnelles, apparue dans une population exposée à un niveau moyen de bruit b décibels (A) pendant la durée (t) années, diffère fondamentalement d'une enquête à l'autre. Le niveau admissible de bruit devient alors imprécis.

Le modèle stochastique compartimental proposé permet d'expliquer ces disparités en s'inspirant d'une méthode épidémiologique qui a fait sa preuve dans le domaine d'une autre maladie professionnelle, la silicose.

Le paramètre fondamental de ce modèle est la probabilité d'aggravation du déficit moyen pratique d'un sujet exposé à un niveau de bruit donné pendant un temps donné. Les déficits auditifs sont regroupés en classes et le modèle s'apparente à un processus markovien de diffusion d'un compartiment dans un autre.

La probabilité ainsi définie est une fonction du niveau moyen de bruit. Elle doit permettre de déterminer la fréquence des surdités à craindre pour une durée d'exposition quelconque et de fixer le niveau moyen admissible de bruit.

La validation du modèle ne pourra se faire complètement qu'au jour où seront connus les résultats de l'enquête entreprise par l'INRS dans l'industrie française: cependant, pour fixer les idées, le modèle a été confronté avec succès avec quelques données actuellement disponibles. Dans ce cadre, une tentative a été faite pour établir la relation entre l'intensité, la sensation sonore et la probabilité d'aggravation du déficit auditif.

ABSTRACT

The results of audiometry and sound-level studies currently available are heterogeneous. In fact, the hearing deficiency threshold, beyond which deafness is considered to exist, varies: 25dB according to ISO standard R/1999 and 35dB in the French table of occupational diseases. The practical mean deficiency itself accords varying degrees of importance to the conversational frequency of 1000Hz. The result is that the frequency F(t,b) of occupational deafness in a section of the population exposed to a mean noise level b in decibels, over a given period of time (t), differs fundamentally from one survey to another. The admissible noise level, therefore, is very flexible.

The proposed compartmental stochastic model provides an explanation of these disparities, based on an epidemiological method which proved useful in the case of another occupational disease, silicosis.

The fundamental parameter of this model is the probability of aggravating the practical mean deficiency in a subject exposed to a given noise level over a given period of time. Auditory deficiencies are grouped according to categories and the model has some points in common with a Markov process of diffusion from one compartment into another.

The probability thus defined is a function of the mean noise level. It should make it possible to determine the frequency of deafness which can be expected for any given period of exposure and to fix a mean admissible noise level.

The model cannot be considered thoroughly tested until the results of the investigation undertaken by the INRS in industry in France are known. However, to obtain an indication of its efficiency the model was used successfully with some currently available data. Within this framework an attempt was made to establish the relationship between intensity, sense of hearing and probable aggravation of auditory deficiency.

1. Introduction

Les examens audiométriques et sonométriques permettent de déterminer le déficit auditif moyen pratique des sujets d'une population exposée à un même niveau de bruit. Celui-ci est malheureusement défini de façons diverses. En France, on considère la moyenne des déficits aux trois fréquences conversationnelles 500, 1000, 2000 hertz en donnant à la seconde un poids double des deux autres. La recommandation ISO R/1999[1] préconise de son côté la moyenne équipondérée des trois déficits. Quand le déficit moyen pratique dépasse une certaine valeur seuil, fixée à 35 dB en France mais à 25dB dans la recommandation ISO, il est convenu d'y voir le signe de la surdité.

Il en résulte que la fréquence F(t,b) des surdités professionnelles apparues dans une population exposée à un bruit de niveau b pendant la durée t diffère fondamentalement d'une enquête à l'autre. Le niveau de bruit admissible devient alors imprécis. Aussi est-il intéressant de rechercher des paramètres liés plus directement à l'étiologie et aux conditions d'apparition de la surdité professionnelle et d'introduire en particulier une notion probabiliste plus fine que la simple prévalence F(t,b).

Dans ce qui suit la population exposée à un certain niveau de bruit b sera décrite au moyen de classes de déficits auditifs limités supérieurement, par exemple, à 15, 25, 35,...dB. L'effectif de chaque classe sera alors l'élément d'une matrice ligne :

$$N(t,b) = (N_1, N_2, \dots, N_k, \dots, N_n)_{t,b} \quad , \qquad (1)$$

indexée par les paramètres t et b. En considérant comme unité l'effectif de la population totale, la prévalence $F_i(t,b)$ des sujets atteints de surdité professionnelle au seuil i de déficit auditif sera égale à :

$$F_i\,(t,b) = \sum_{j=i}^{j=n} N_j \qquad (2)$$

L'incidence pourra être représentée par la probabilité $\Pi_i(t,b)$ dt de présenter une surdité entre les époques t et (t+dt) pour un sujet que l'on sait non atteint à l'époque t :

$$\Pi_i(t,b)\ dt = \frac{dF_i(t,b)}{1 - F_i(t,b)} = \frac{dZ_i(t,b)}{dt} \qquad (3)$$

où $Z_i(t,b)$ est la fonction auxiliaire $\quad \text{Log} \dfrac{1}{\left(1 - F_i(t,b)\right)} \qquad (4)$

Les figures 1 et 2 donnent les valeurs de F_i et Z_i pour deux enquêtes, d'une part celle de MORIN[2] portant sur 149 forgerons exposés à des bruits de 100 dB environ avec des pointes fréquentes à 115 ou 120 dB (i = 1,2,3 correspondant à des seuils de 15, 25, 35 dB), d'autre part celle de la re- ...

PREVALENCE DE LA SURDITE AUX SEUILS 15,25,35 dB
EN FONCTION de la DUREE d'EXPOSITION
POUR UNE MEME AMBIANCE SONORE
(D'après les résultats de J. MORIN)

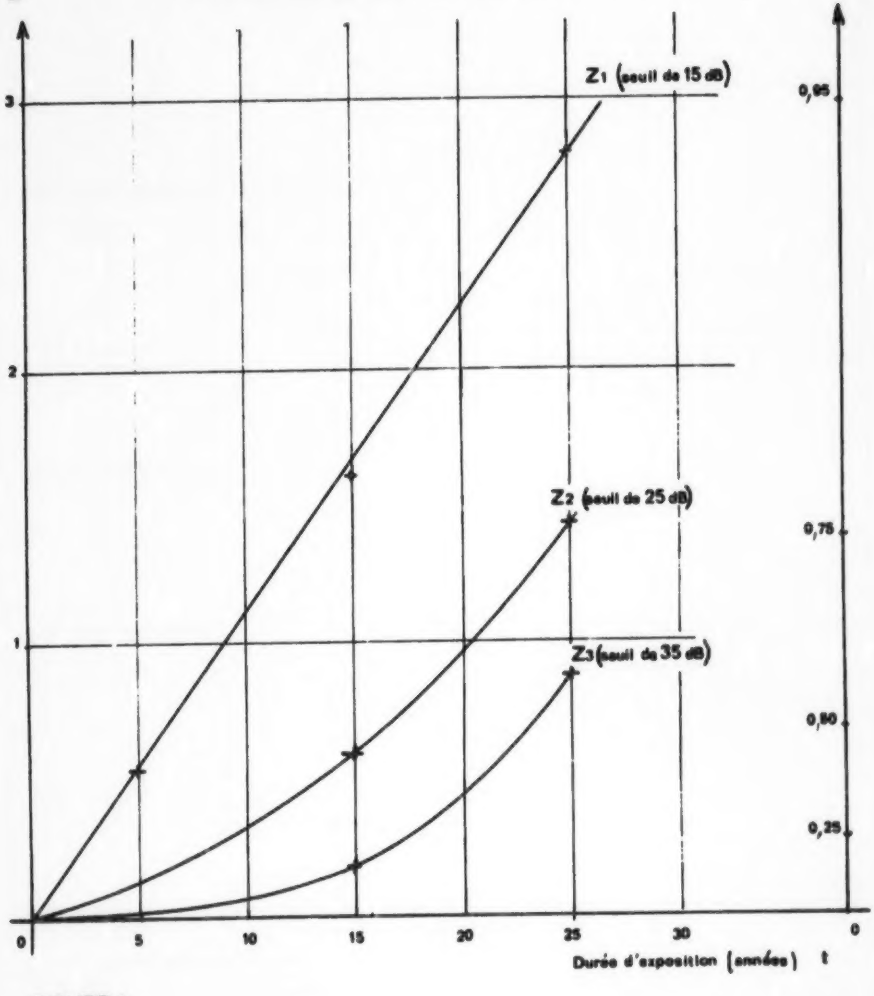


FIGURE.1

PREVALENCE DE LA SURDITE AU SEUIL 25 dB EN FONCTION DE LA DUREE D'EXPOSITION ET DU NIVEAU MOYEN DU BRUIT

(D'après les résultats d'enquêtes contenus dans la Recommandation I.S.O R/1999)

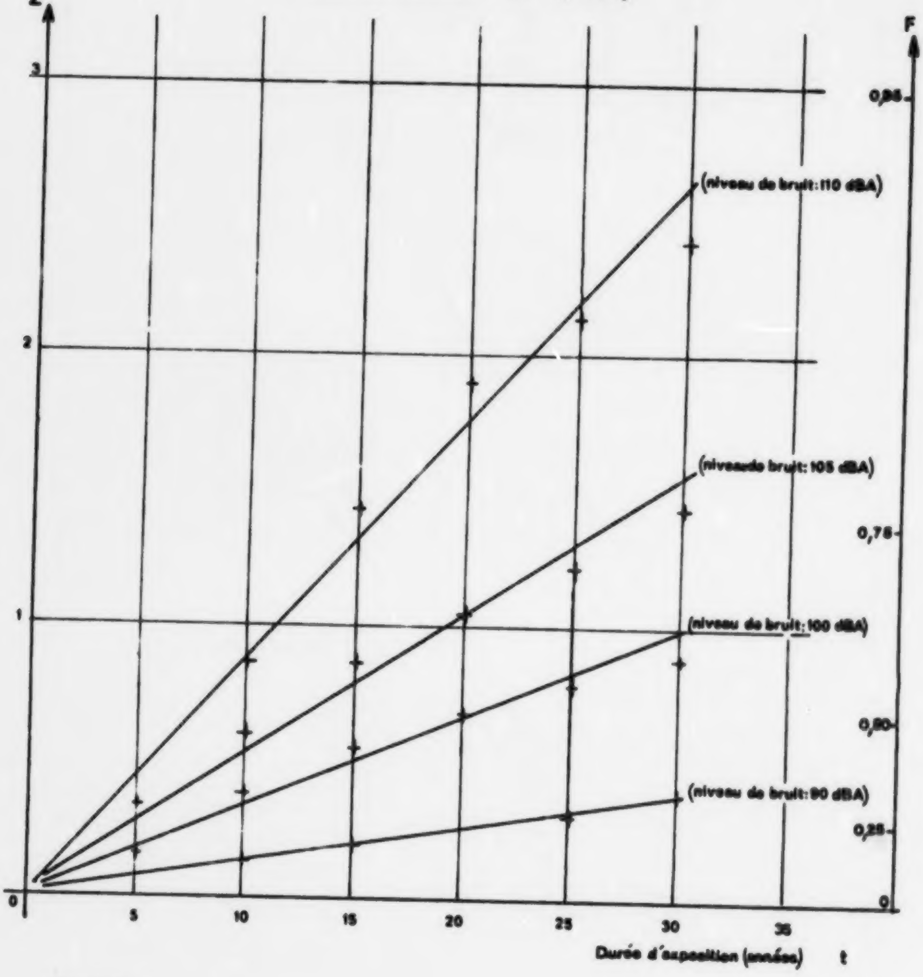


FIGURE 2

commandation ISO R/1999 ($i = 1$ correspondant au seuil de 25 dB ; $b = 90, 100, 105, 110$ dBA).

La probabilité par unité de temps $\Pi_i(b,t)$ varie avec le temps d'exposition et le niveau b, sauf d'ailleurs pour de faibles valeurs de seuil.

Le but du modèle proposé est de déterminer une probabilité élémentaire qui rende compte des valeurs de $F_i(t,b)$ et $Z_i(t,b)$, tout en ne dépendant que de b.

2. Modèle stochastique compartimental

Le modèle qui suit est donné à priori. Il sera justifié ultérieurement par ses conséquences et par la comparaison avec les données des enquêtes audiométrie-sonométrie.

L'état d'une population à l'instant t étant caractérisé par la matrice ligne $\left[N(t,b)\right]$:

$$\left[N(t,b)\right] = (N_1, N_2, N_3, \ldots, N_k, \ldots, N_n)\ t,b \qquad (5)$$

on suppose que la probabilité de passage de la classe de déficit auditif k à la classe suivante (k+1) (probabilité d'aggravation) entre les époques t et (t+dt) est égale à $p_k(b)\,dt$. Cette quantité est une fonction du rang de la classe de départ et du niveau moyen de bruit auquel a été exposé le sujet. Tout se passe dans ce modèle comme si tous les sujets placés à l'époque t dans le compartiment correspondant à la classe k de déficit auditif "diffusaient" entre t et (t+dt) dans le compartiment k+1 (et non dans un autre) avec la probabilité $p_k(b)dt$. Le processus de changement d'état de la population exposée au bruit est continu, stochastique et markovien. Dans le cas où $p_k(b)$ est indépendant de k, il est de plus poissonnien. Il sera démontré d'ailleurs que l'examen de ce cas particulier est pratiquement suffisant. Les sujets sont répartis entre les différents compartiments suivant une distribution d'ERLANG généralisée. La probabilité $a_k(t,b)dt$ pour un sujet d'atteindre le compartiment k entre les époques t et (t+dt) est définie par le produit de composition :

$$a_k(t,b) = \int_0^t a_{k-1}(\tau,b)\, d\tau \,.\, e^{-p_{k-1}(t-\tau)} , \qquad (6)$$

somme des produits de la probabilité d'atteindre le compartiment k-1 entre les époques τ et $\tau+d\tau$ par celle de le quitter au terme d'une période comprise entre $(t-\tau)$ et $(t+dt-\tau)$.

Ces produits de composition sont facilement calculables dans le cas poissonnien où $p = p_1 = p_2 = \ldots = p_k = \ldots$ (distribution d'ERLANG classique) :

$$a_k(t,b) = \frac{1}{(k-2)\,!}\, p^{k-1}\, t^{k-2}\, e^{-pt} , \quad (k > 1), \qquad (7)$$

...

Le nombre de sujets qui, à l'époque t, n'ont pas atteint le compartiment k est égal d'une part à la somme $N_1(t,b) + N_2(t,b) + \ldots + N_{k-1}(t,b)$ et d'autre part à :

$$\int_t^\infty a_k\ (t,b)\ dt \tag{8}$$

On tire de cette égalité la valeur de $N_k(t,b)$:

$$N_k(t,b) = \int_t^\infty \left(a_{k+1}(t,b) - a_k(t,b)\right) dt\ , \tag{9}$$

avec $N_1(t,b) = e^{-p_1 t}$.

Dans le cas poissonnien, il vient en particulier :

$$N_2 = e^{-pt}\ pt \quad ; \quad N_3 = \frac{1}{2!}\, e^{-pt} p^2 t^2 \ldots \tag{10}$$

Dans le cas général, on montre que les valeurs données par (9) diffèrent peu de (10) tant que les écarts de p_k à leur moyenne p sont faibles. Aussi les (10) pourront-elles être utilisées en première approximation pour déterminer la fréquence des surdités dans chacun des compartiments k à l'époque t.

En fixant le seuil de surdité entre les classes de déficit auditif k et k+1 et en posant X = pt, la fonction Z s'écrit :

$$Z_k = X - \text{Log}\ \left(1 + X + \frac{1}{2!} X^2 + \ldots + \frac{1}{(k-1)!}\ X^{k-1}\right) \tag{11}$$

Il vient en particulier :

$$Z_1 = X \qquad Z_2 = X - \text{Log}(1+X) \qquad Z_3 = X - \text{Log}(1+X+ \frac{1}{2} X^2) \tag{12}$$

et en inversant les fonctions Z_1, Z_2, Z_3 :

$$X = \Phi_1(Z_1) = \Phi_2(Z_2) = \Phi_3(Z_3) \tag{13}$$

3. Validation du modèle

Le modèle ci-dessus pourra être validé quand l'Institut National de Recherche et de Sécurité sera en possession des résultats de l'enquête audiométrie-sonométrie qu'il a entreprise. Il en sera de même du choix des compartiments en nombre et en extension. Cependant, il est intéressant de préciser la méthode de validation en utilisant les résultats des enquêtes citées au § 1.

Dans le travail de Morin, en adoptant quatre compartiments (0-15, 15-25, 25-35, 35 dB et plus), on constate que les relations (13) sont vérifiées quels que soient i et t pour une même valeur de p égale à 0,11. Ainsi, les courbes expérimentales Z et F de la figure 1 sont correctement interprétées avec le seul paramètre p qui caractérise le niveau de bruit décrit. Les résultats obtenus à partir de la recommandation ISO R/1999 sont d'un autre ordre. La forme quasi linéaire des courbes de la figure 2 montre en effet qu'au seuil 25 dB et avec la définition du déficit auditif

...

pratique adopté par l'ISO $\Pi_i(t,b) = dZ/dt$ ne dépend que de b, ce qui permet de prendre 25 dB comme limite du premier compartiment ($i=1$). La définition du déficit pratique moyen de cette Recommandation donne à la fréquence 2000 hertz un rôle prépondérant. On sait par ailleurs que c'est au voisinage de cette fréquence qu'apparaissent les troubles auditifs précoces (dans la gamme 500 à 2000 hertz). Aussi, ne faut-il pas s'étonner si les compartiments qui rendent compte de la prévalence en fonction de la durée d'exposition sont différents de ceux qui ont été utilisés dans l'enquête de MORIN.

La figure 3 montre d'autre part que $\Pi_{25\ dB}(t,b) = p(b)$ dépend de b, en suivant une loi logarithmique :

$$\text{Log } p(b) = Ab + B \,, \qquad (14)$$

où A et B sont des constantes respectivement égales à 0,0389 et − 5,414.

En revenant à la définition du décibel en fonction de l'intensité sonore I et de l'intensité de référence I_o (10^{-16} watts/cm^2), la relation (14) s'écrit pour un bruit de 1000 Hz :

$$p(b) = 3{,}9 \times 10^{-6} \times (I/I_o)^{0{,}39} \qquad (15)$$

Les probabilités p(b) d'apparition ou d'aggravation sont multipliées par 2,5 environ quand l'intensité est multipliée par 10. La relation (12) exprimant $Z_i(t,b)$ en fonction du produit p.t, diviser p(b) par un coefficient k et multiplier simultanément t par le même coefficient ne change pas la prévalence, quel que soit d'ailleurs i. En tenant compte de (14), on pourra donc écrire :

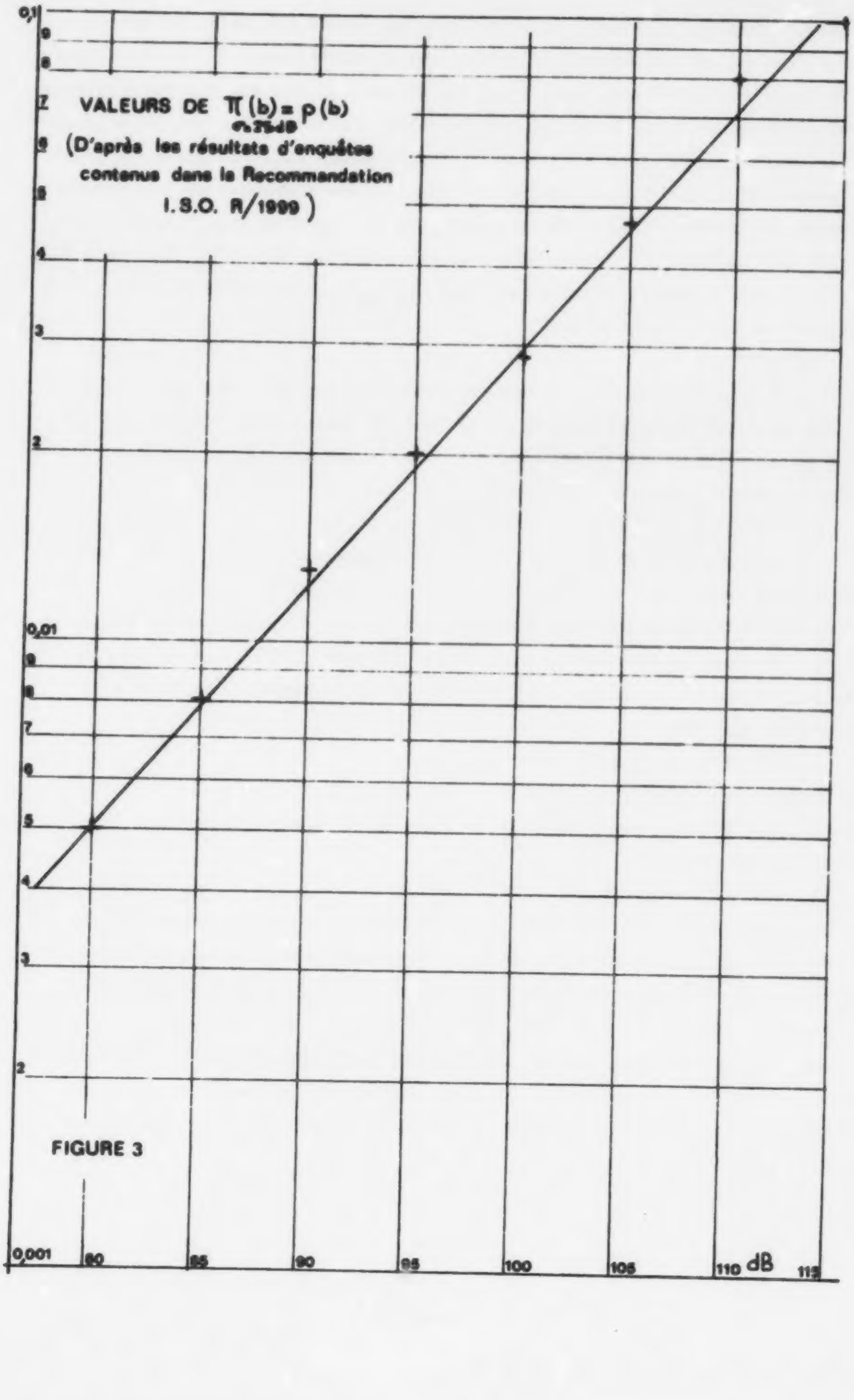
$$Z_i(t,b) = Z_i\ (t \times 2{,}5^n \,,\ b - 10n) \qquad (16)$$

Depuis les travaux de STEVENS il est admis que la sensation sonore (sonie) varie comme une puissance de l'intensité sonore, soit pour un bruit de 1000 Hz [3] et [4] :

$$S = 10^{-1{,}2}\ (I/I_o)^{0{,}3} \qquad (17)$$

La comparaison de (15) et (17) montre que la sensation sonore et la probabilité p(b) sont proportionnelles en première approximation. Cette relation est satisfaisante pour l'esprit et donne un sens intrinsèque à la probabilité p(b).

La limite supérieure du niveau moyen de bruit admissible sera déterminée à partir des résultats d'une enquête extensive en choisissant l'endémie résiduelle acceptable, AMOUDRU [5], HO et QUINOT [6].



VALEURS DE $\underset{\sigma=7,5\,dB}{\Pi(b)} = p(b)$
(D'après les résultats d'enquêtes contenus dans la Recommandation I.S.O. R/1999)

FIGURE 3

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EVALUATION DE LA CHARGE CORPORELLE EN MERCURE PAR SIMULATION NUMERIQUE

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RESUME

On évalue la quantité de méthyle de mercure et de mercure inorganique absorbée par la population après consommation de poissons. A partir des analyses effectuées sur les poissons marins pêchés en Europe, on prend comme teneur médiane 0.3 et 0.7 ppm de mercure total, les trois quarts de la concentration en mercure étant sous forme méthylée. L'évaluation tient compte aussi de la consommation de poissons. Elle est simulée de deux façons à partir des enquêtes alimentaires effectuées antérieurement, d'une part, en fonction de l'âge des consommateurs, d'autre part, en prenant une distribution de la consommation par repas répartie normalement autour d'une valeur moyenne. Dans ce cas, on étudie l'influence de la fréquence de consommation du poisson, elle est introduite dans le calcul sous forme de variable aléatoiresimulant les cas de consommations rapprochées ou espacées. Pour calculer la charge corporelle dans ces divers cas en fonction du temps, on utilise un modèle à un seul compartiment pour l'absorption du méthyle de mercure (absorption 100%, période 70 jours) et pour la forme inorganique (15%, période 15 jours). Les niveaux decontamination et leurs amplitudes de variation sont discutés, dans un certain nombre de cas traités par simulation numérique sur calculateur, les charges corporelles en mercure diffèrent par un facteur de sécurité inférieur à dix en regard des niveaux toxiques répertoriés au Japon.

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ABSTRACT

An assessment is made of the amount of methylmercury and inorganic mercury the population absorbs by eating fish. Using analyses carried out on European salt-water fish as a basis, the median content is taken to be 0.3 and 0.7 ppm total mercury, three-quarters of the mercury concentration being in the methyl form. The assessment also takes account of fish consumption which is simulated in two ways, using previous surveys of food consumption: firstly in terms of the age of the consumer and secondly using consumption distribution by meal based on an average value. In this case the effect of the frequency of fish consumption is studied, and is introduced in the calculation in the form of a random variable simulating consumption at frequent or infrequent intervals. In order to calculate the time-dependent body burden in the various cases a model with a single compartment is used (absorption 100%, period 70 days) for methyl mercury absorption, and, for the inorganic form, (15%, period 15 days). Contamination levels and their range of variation are discussed and in certain cases processed by digital simulation by computer; the mercury body burdens differ from the toxic levels recorded in Japan by a safety factor of less than ten.

INTRODUCTION

Le phénomène de concentration d'un certain nombre de polluants métalliques et organométalliques dans les divers maillons de la chaîne alimentaire jusqu'à l'homme, a été particulièrement bien montré pour le mercure. Même si le rejet de ce polluant n'entraîne de nuisances qu'à une échelle locale, la toxicité du méthyle de mercure est suffisamment sévère à faible teneur pour justifier une étude générale de la charge corporelle après ingestion de ce composé. De toute façon, il y a désaccord entre les auteurs, sur la quantité du mercure qui est sous forme méthylée dans l'organisme (1) (2). Nous sommes essentiellement guidés dans ce travail par l'approche qu'en ont fait, pour la première fois SPEAR et WEI (3) en proposant une étude simulée pour calculer le résidu de méthyle de mercure restant dans l'organisme. On se propose de généraliser cette méthode à la fraction organique et inorganique du mercure tout en n'envisageant, comme ces auteurs, que le poisson comme seul vecteur de contamination. Nous utilisons, pour cela, une méthode de simulation numérique sur calculateur digital (4).

Hypothèses utilisées

La courbe de répartition de la teneur du mercure dans le poisson est proche d'une distribution log normale. Nous préférons introduire une distribution observée par CUMONT (5) sur 360 poissons. La teneur médiane en mercure est 0.3 ppm (Fig. 1). Cette même distribution a été utilisée avec une teneur médiane de 0.7 ppm. Dans tous les cas, la fraction méthylée représente 75% de la teneur en mercure.

La consommation de poisson par repas est représentée par une loi normale dont la valeur moyenne est 200 g et l'écart type 40 g. La fréquence de consommation du poisson est introduite dans le calcul, sous forme de loi binomiale avec $p = q = 1/2$; la valeur médiane représente les cas de consommation rapprochée (2 repas par semaine), normale (1 repas par semaine), espacée (1 fois par mois).

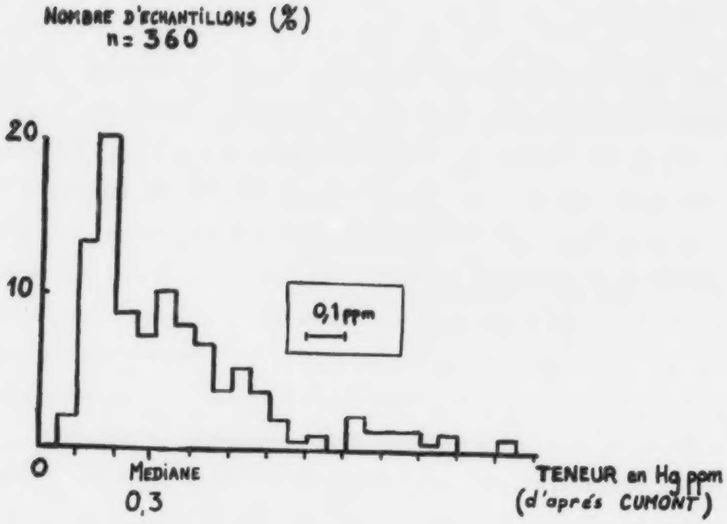


Fig. 1 REPARTITION DES TENEURS EN MERCURE DANS LE POISSON.

Pour une région fortement consommatrice, nous avons d'une part, utilisé la quantité consommée en fonction de l'âge, de l'ordre de 75 g/jour (6, 7) d'autre part, 250 g de poisson par repas, le même écart type et 2 repas par semaine. Le modèle métabolique ne met en jeu qu'un seul compartiment Le méthyle de mercure est absorbé à 100%, et sa période biologique est de 70 jours, le mercure inorganique est absorbé à 15% et sa période biologique est de 15 jours.

Evaluation de la charge corporelle

La variation de la charge corporelle de 6 individus est suivie sur une période de deux années (Fig. 2). L'équilibre est pratiquement atteint au bout de 150 jours dans tous les cas, mais les écarts entre les teneurs minima et maxima atteignent 35%, 10% provenant de la dispersion des concentrations en mercure dans le poisson.

Le cas d'une région fortement consommatrice a été étudié à partir des données de CRESTA sur la Vendée (France) (7) le niveau critique atteint est discuté par la suite.

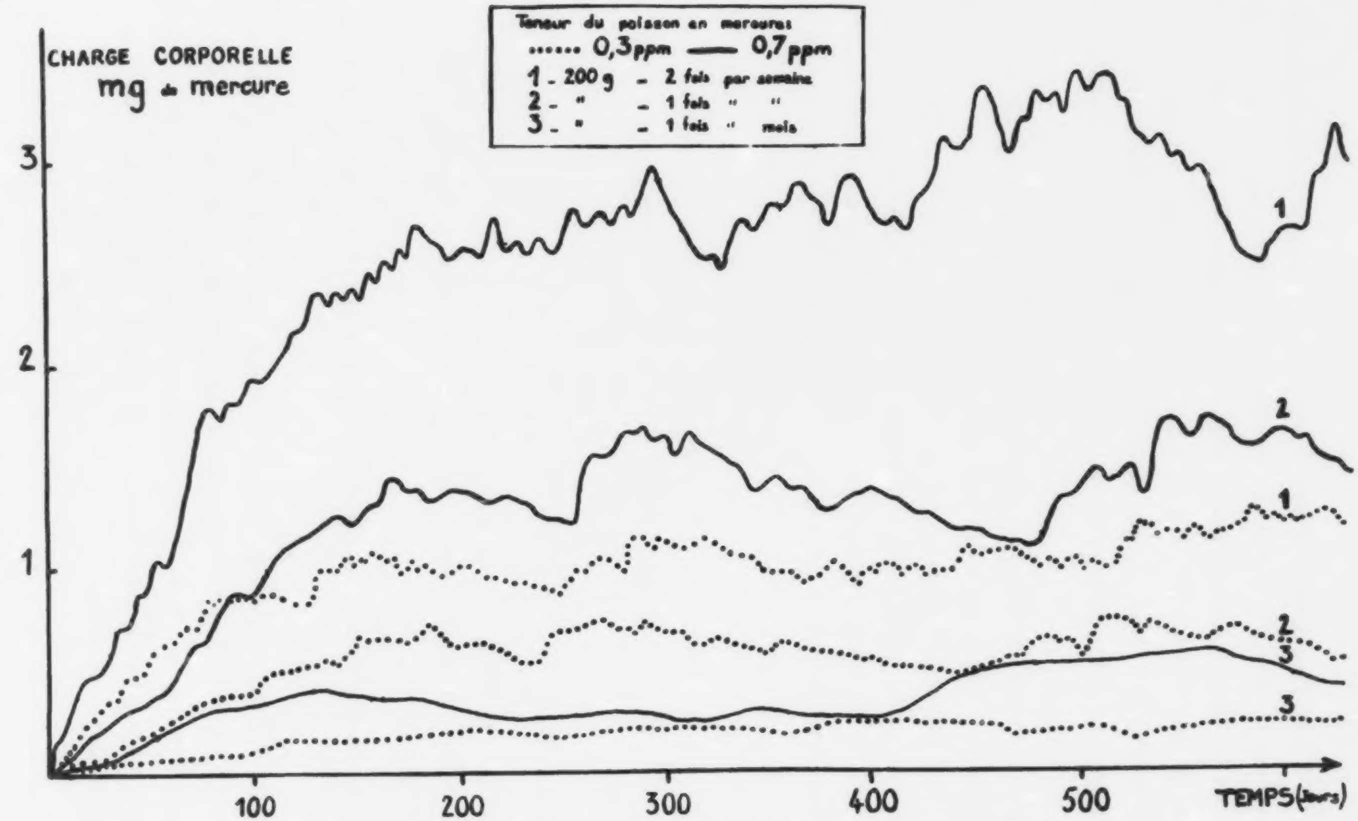


Fig. 2 VARIATION DE LA CHARGE CORPORELLE EN FONCTION DU TEMPS.

Charge corporelle et niveaux toxiques

WEI et SPEAR (8) ont déterminé la charge corporelle totale correspondant aux teneurs en mercure relevées sur différents échantillons biologiques de onze cas en début d'intoxication ultérieurement létale: 54 mg, 87 mg, 90 mg, 91 mg, 94 mg, 114 mg, 118 mg, 118 mg, 165 mg, 292 mg, 292 mg et d'autres cas de troubles nerveux correspondant à une charge corporelle de 60 mg. En appliquant un facteur de sécurité de 10, la charge corporelle critique sera de 5.4 à 6 mg.

La recherche des maxima de charge corporelle en mercure sur un échantillon de population de 1000 individus dont la quantité hebdomadaire ingérée correspond à la dose tolérable de 0.3 mg proposée par l'O.M.S. (9), nous montre qu'un individu sur mille atteint une valeur proche de la charge critique, soit 5.2 mg (Fig. 3). Dans tous les autres cas, elle est très inférieure. On a vu que le niveau critique égal ou supérieur à 6 mg est atteint pour une région fortement consommatrice (7) et pour une teneur en méthyle de mercure de 0.75 ppm dans le poisson. L'extension du modèle à la ration complète (10) entraînerait un doublement de l'ingestion du mercure total (11) mais la forme inorganique y est prépondérante (12) et on a vu qu'elle est rapidement éliminée.

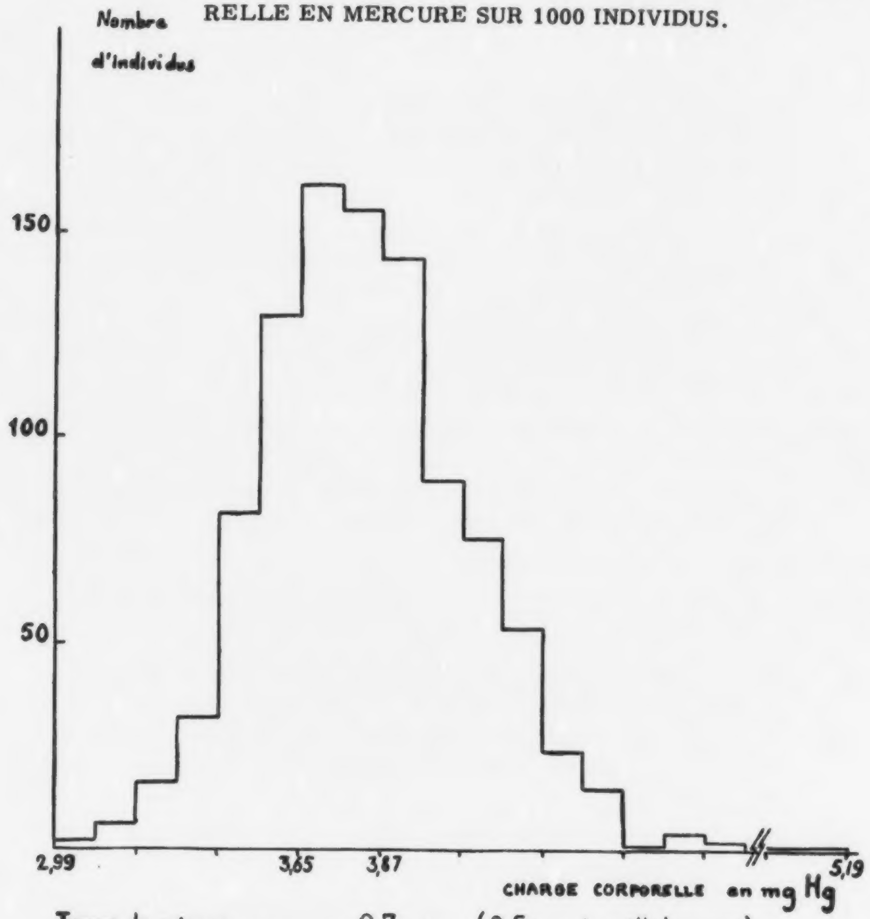
CONCLUSION

Nous avons calculé la charge corporelle en mercure, résultant de l'ingestion de poisson en tenant compte de la distribution statistique d'un certain nombre de paramètres:

teneur du poisson en mercure, quantité ingérée par repas, espacement des repas.

Par cette méthode, nous avons mis en évidence une amplitude de variations de la quantité de mercure retenue de 35% chez le même individu. La charge corporelle en méthyle de mercure est prépondérante et l'extension du modèle à la ration complète ne modifierait pas sensiblement les valeurs obtenues pour cette forme chimique.

Fig. 3 REPARTITION DES MAXIMA DE LA CHARGE CORPORELLE EN MERCURE SUR 1000 INDIVIDUS.



Teneur du poisson en mercure : 0,7 ppm (0,5 ppm de méthylmercure)
Consommation : 200 g - 2 fois par semaine
Charge corporelle maximum : médiane 3,7 mg dont 3,65 mg de méthylmercure

La recherche des maxima sur un échantillon de 1000 individus consommant du poisson deux fois par semaine en moyenne, contenant 0.7 ppm de mercure, montre qu'une charge corporelle de 5.2 mg est atteinte avec une fréquence de 1/1000 alors que les cas d'intoxication ont été observés pour une charge estimée de 54 à 60 mg.

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THE USE OF CANADIAN MEDICARE DATA IN DEFINING HEALTH EFFECTS OF THE ENVIRONMENT ON MAN

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ABSTRACT

With the development of computer technology health data can be used to identify effects of the environment on health. The Canadian medicare data base, comprised of provincial components, is composed of the number, cost and diagnostic code of the physician services that each resident receives. Analysis of such computerized information allows comparison to be made between populations with regard to the number and cost of physician services for defined diagnostic codes or code groupings.

Saskatchewan medicare data has been used to define the effects of the agricultural environment on health with particular reference to accidents and the effects of agricultural machinery, grain dust and agricultural chemicals. Medicare data was used to identify 112 persons treated for methomyl intoxication in 1971; subsequent interview of the physician and patient allowed for the evaluation of diagnosis and insecticide-handling practices.

The main limitation to the use of medicare data stems from the fact that health insurance agencies may have no defined responsibility for the preventive aspects of health care and therefore no commitment to make full use of their data to define health effects of the environment on man.

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The use that can be made of medicare data to define the effects of environment on health appears initially to be dependent not only on the ability to precisely define a particular health hazard and the resulting health effect, but also on the uniqueness of the health effect. Medicare data has special value where precise definitions cannot be formulated but where the data can still be used to support, or not, a hypothesis that a particular environmental hazard contributes to the incidence of a health effect in a population.

1. INTRODUCTION

While most health agencies necessarily have been governed by economic interests in the design and utilization of their health data bases, nevertheless it is becoming apparent that with the development of computer technology, this same information can also be used to identify health problems which may, upon evaluation, contribute to a greater understanding of environmentally induced health effects.

The characteristics of optimum quality health (and accident) statistics may be enumerated as follows:

(a) The information on which the statistics are based should be true.

(b) The statistics should relate to total populations.

(c) The statistics should be detailed enough to identify problem areas but simple enough to ensure assembly.

(d) The statistics should allow access back to individual records for detailed evaluation of problem areas.

(e) The statistics should allow valid comparisons to be made with regard to time, place and population.

Canadian medicare data, particularly the data from Saskatchewan, possesses in large measure the characteristics outlined.

2. HEALTH CARE DATA IN CANADA

Canada has a national health care data base composed of various provincial components. All provinces produce certain information which is somewhat comparable such as in the area of vital statistics. Hospitalization data are also compiled nationally.

The advent of universal medical care insurance coverage in Canada created a vital component in the health care data base in regard to the definition of environmentally induced health effects. Basically, whenever an insured resident receives a physician's service the physician is required to identify the diagnosis on a billing card which he renders to the provincial insurance agency in order to get paid. Information relating to each service becomes a part of that person's "patient history file". In a given population the patient history files include a record of the number, cost and diagnostic codes of physician service to that population. In addition they will indicate where the services were provided as well as individual characteristics of each patient and allow comparison with other populations. Each province produces statistics from the medicare system for its own purposes as well as to satisfy federal requirements. Some produce more than others and some have it stored over a longer period of time. The province of Saskatchewan has been a pioneer in the field of health care delivery systems in Canada and medicare data have been computerized since 1962 in that province. Use has been made of it in defining the effects of the agricultural environment on farmers with particular reference to accidents; tractor vibration and tractor noise; the effects of continued exposure of grain buyers to grain dust; and the evaluation of the acute toxic effects of certain agricultural chemicals.

3. EXAMPLES OF THE USE OF SASKATCHEWAN MEDICARE DATA

3.1 Toxic effects of methomyl. In 1971, when a heavy infestation of the Saskatchewan rape seed crop by the Bertha army-worm necessitated the widespread use of the insecticide "methomyl", a project was designed to identify and evaluate cases of methomyl intoxication. A computer program modification was introduced for three weeks which identified all physician service claims for Code 989 (ICDA - eighth rev.). Cards were then scanned manually to identify claims for methomyl intoxication and 112 persons were identified. Each patient and the attending physician was subsequently contacted personally for evaluation of exposure, diagnosis, effect and treatment. A similar program was carried out in 1972 but for a longer period of time. 19 patients were identified in the first three weeks, 38 in total. The program not only allowed speedy identification of patients, (3-4 weeks from date of physician service to computer identification) but also allowed for the evaluation of causes of illness and insecticide-handling practices.

3.2 Health of Farmers. Health surveys of farmers in Saskatchewan have indicated a positive correlation between hearing loss, back disorders, accidents; and increasing farm size (which implies increased use of farm machinery). An evaluation of medicare data using a random sample of Saskatchewan farmers supports the hypothesis that increased exposure to farm machinery is associated with increasing number and costs of total physician services (Table I) and services relating to specific health effects.

4. DISCUSSION

While the value of health statistics derived from medicare data obviously depends upon the ability and efficiency of the physician who is providing the diagnosis, it should also be noted that they are based upon information recorded for payment purposes. Thus, where a choice

TABLE I

NUMBER AND COST OF PHYSICIAN SERVICES TO FARMERS BY AGE AND SPECIFIED FARM SIZE, 1963-1969 INCLUSIVE.

Age Group (in 1969)	Number of Farmers		Number of Services per Farmer		Cost of Services per Farmer	
	< 900 acres	900 + acres	< 900 acres	900 + acres	< 900 acres	900 + acres
25-34	458	49	17.9	17.9	$118.00	$115.40
35-44	691	163	21.7	23.9	145.20	168.60
45-54	921	173	24.0	26.2	165.40	163.90
55-64	734	73	28.2	39.9	189.20	276.20
65 and over	437	17	36.0	44.7	263.00	342.90

NOTE: 1 acre = .405 hectare

must be made between two legitimate diagnoses and their treatments, a decision may be made for economic reasons which may prove misleading for research purposes; by using large populations these research limitations are minimized. A further limitation to the use of medicare data is that only one diagnosis is recorded for payment purposes and a decision often must be made among several reasonable possibilities. The most important limitation stems from the fact that often the health insurance agencies have no direct responsibility for the preventive aspects of health so that the commitment to make available medicare data to define the interactions between man and his environment may be absent.

Notwithstanding the limitations, this data source has great potential in defining man/environment effects, particularly when the health characteristics of different populations need to be compared to identify the health aspects. For example, health effects associated with increasing population size and density: infectious and parasitic diseases, accidents and poisonings, congenital anomalies and various health effects peculiar to occupational groups. (Table II.)

The use that can be made of medicare data to define the effects of environment on health appears at first glance to be dependent not only on the ability to precisely define a particular health hazard and the

TABLE II

COST OF INSURED SERVICES PER 1000 PERSONS (CANADIAN $)
FOR SELECTED DIAGNOSTIC CATEGORIES AND SELECTED POPULATIONS,
SASKATCHEWAN MEDICAL CARE INSURANCE COMMISSION, 1971.

DIAGNOSTIC CATEGORY	RESIDENCE GROUPS		
	RURAL (POP. 253,822)	2 MAJOR CITIES (POP. 267,328)	REGISTERED INDIANS (POP. 33,478
	$	$	$
I Infectious & parasitic diseases	719	1,113	3,616
V Mental Disorders	825	3,183	809
XIV Congenital Anomalies	286	521	529
XVII Accidents, Poisonings, etc.	2,598	2,952	5,242
TOTAL SERVICES	29,863	48,466	43,552

resulting health effect, but also on the uniqueness of the health effect. While precision is to be desired, the special value of medicare data is particularly apparent where precise definitions cannot be formulated and where the data can still be used to support (or not, as the case may be) a hypothesis that a particular environmental hazard contributes to the incidence of a health effect (or type of health effect) in a population.

I wish to acknowledge the co-operation of the Saskatchewan Medical Care Insurance Commission and its staff for facilitating my research into the use of medicare data in defining the effects of the environment on health.

THE RELATIONSHIP BETWEEN LEAD AND HYPERACTIVITY

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ABSTRACT

Hyperactive children were compared with a non-hyperactive control group on two measures that reflect the presence of body lead - blood-lead levels and urine levels after challenge by a single oral dose of the chelating agent penicillamine. Hyperactive children had significantly higher values on both measures than did the controls. More than half the hyperactive children had blood-lead levels in the range considered to be raised but not "toxic", and 60% of post-penicillamine urine levels were in the "toxic" range. It is concluded that there is an association between hyperactivity and raised lead levels; that a large body-lead burden may exert consequences that have been hitherto unrealized; that the definition of what is a toxic level for blood-lead needs re-evaluation; and that physicians should look for raised lead levels in children with hyperactivity.

Introduction

As most readers know, hyperactivity is one of many terms used to describe a complex, multifaceted syndrome. It is characterized by the fundamental behavioral manifestation of a high level of motor activity and is usually coupled with a short attention span, low frustration tolerance and hyperexcitability.

The question of causality regarding hyperactivity is quite fluid. Retrospective studies commonly show that hyperactive children have in their background a much higher incidence of such events as abnormalities in the mother during the gestational period; difficult delivery histories; and postnatal difficulties such as head trauma, encephalitis, meningitis and other encephalopathies. Prevalence estimates of this and closely related disorders vary, but if we hew closely to the prevalence of hyperactivity per se, approximately 5% of children in the U.S. alone may be suffering with this disorder.

The literature on lead, before our work, contained much that indicated a lively suspicion held by many authorities regarding associations between minor brain dysfunction and low lead levels. It was clear, however, that no study provided a definitive answer to the question: Is there a relationship between asymptomatic lead poisoning or lead poisoning less severe than that causing encephalitis, and mental impairment?

Our investigation was designed to answer as well as we could the following question: Do hyperactive children have larger body lead stores than non-hyperactive controls? The operational hypotheses tested were (1) Hyperactive children will have significantly higher blood lead levels than non-hyperactive controls; and (2) Hyperactive children after challenge by a heavy metal chelating agent will have dramatically higher urine lead levels than controls subjected to the same challenge.

Patients and Methods

Children were classed as hyperactive or non-hyperactive on the basis of a doctor's diagnosis, a teacher's rating scale (the Conners[1] scale) and a parent's rating scale (the Wherry[2]-Weiss-Peters scale). If the three indices were not in accord, the two scores that did agree were used to designate the child hyperactive or non-hyperactive. If only two scores were available, the teacher's scale and then the doctor's diagnosis took precedence, in that order.

Those children who were diagnosed as psychotic or who had evidence of significant neurological disease were excluded from this study. Children with hyperactivity and an event in their background thought to be a cause of this condition were considered separately from those with no such history. These events were broken into "possible" causes and "highly probable" causes, and these groups were analyzed separately. Utilizing the above exclusion process, the following groups emerged: (1) A hyperactive group without psychosis or neurological disease and with no evidence of an event known to be associated with the development of hyperactivity ("pure" hyperactive); (2) The hyperactive group with a "highly probable" cause for their hyperactivity; (3) The hyperactive group with "possible" cause for their hyperactivity; and (4) A group of children whose highly probable cause for hyperactivity was a history of lead poisoning. All children in this group had been treated at least five years previously (with one exception). Five of the eight children in this group were just hyperactive, three had neurological conditions of mild-to-moderate diffuse brain damage, one with mental retardation.

The fifth group was a non-hyperactive control group who were judged on the same criteria as that for the hyperactive group. (See Table I)

Blood lead determinations (two) were done by the New York City Board of Health lead laboratory by the atomic absorption method of Hessel.[3] Urine lead levels were done by the same laboratory on an overnight sample collected after a 250 mgm Penicillamine provocation dose.

TABLE I - DETAILS OF GROUPS STUDIED

Group	No.	Age (yr.)			M/F	Mean hyperactivity score	
		Mean	S.D.	Range		Teacher	Parent
"Pure" hyperactive	54	7.8	2.04	3½-11	43/12	3.2	3.2
Highly probable cause for hyperactivity	9	7.3	2.25	4-10	8/1	2.8	2.7
Possible cause for hyperactivity	11	7.7	1.28	6-10	9/2	3.1	2.1
History of lead poisoning	8	7.3	1.73	3½-9	8/0	3.5	3.4
Controls	37	7.6	2.14	3½-12	27/10	1.6	0.8

Results

Results comparing the normal control group to each of the four hyperactive groups is presented in Table II. Mean differences in blood and urine lead levels between the controls and 3 of the 4 hyperactive groups show that the non-hyperactive children have significantly lower blood and urine lead levels than do the hyperactive subjects.

The exception to this was the lead levels in the highly probable cause group. On the two measures utilized, they showed no significant difference from the controls.

The range and frequency distribution of these findings are present in Table III, in the light of what is now considered to be normal, marginal and toxic levels. A normal blood lead value is here defined as 24.5 ug/100 ml or less. A normal urine lead level is defined as 80 ug/liter or less.

TABLE II--BLOOD-LEAD AND POST-PENICILLAMINE URINE LEAD LEVELS IN FOUR GROUPS OF HYPERACTIVE CHILDREN COMPARED WITH NON-HYPERACTIVE CONTROLS

Group	Blood-lead			Post-Penicallimine urine lead		
	No. tested	Mean S.D. (ug./100 ml.)	p*	No. tested	Mean S.D. (ug./l.)	p*
"Pure" hyperactive	54	26.23±8.41	< 0.01	50	146±144	< 0.02
History of lead poisoning	8	41.06±12.18	< 0.001	4	325±167	< 0.00
Highly probable cause of hyperactivity	9	22.89± 6.60	N.S.	5	46±32	N.S.
Possible cause for hyperactivity	8	29.94±7.35	< 0.01	9	189±155	< 0.01
Controls	37	22.16±9.59	..	24	77±92	..

*Student's t test (one tail).

An examination of Table III shows that for the normal control Ss 73% had "normal" blood lead levels and 27% were in the "elevated" range. In the "pure" hyperactive group 52% showed elevated blood lead values and 48% were in normal range. A chi square analysis with one degree of freedom indicates that the probability of this frequency happening by chance is less than .02. Post-penicillamine urine lead scores for these two groups show that 62% of hyperactive children had elevated lead levels while only 21% of the controls had elevated levels. 79% of the normal Ss had urine levels within normal limits while this was true for only 38% of the "pure" hyperactive Ss. A chi square analysis indicates that the probability of this occurring by chance is less than .001.

The frequency analysis of blood lead levels and urine lead levels for the "possible" cause group was as follows: 62-1/2% had elevated blood lead scores and 78% had elevated urine lead scores (See Table III).

The last group compared to the normal controls is the hyperactive group whose "highly probable" reason for the hyperactivity is a documented past history of overt lead poisoning. The frequency of blood and urine lead scores shows that 100% have elevated post-penicillamine urine lead scores.

TABLE III--FREQUENCY OF RAISED BLOOD-LEAD AND POST-PENICILLAMINE URINE-LEAD LEVELS

Group	No. of children with blood-lead levels (ug./100 ml.) in range:						No. of children with urine (ug./l) in range:			
	5-14-5	15-24-5	25-34-5	35-44-5	45-54-5	55-64-5	0-80	81-160	161-240	> 241
"Pure" hyperactive	4 (7%)	22 (41%)	19 (35%)	7 (13%)	2 (4%)	0	19 (38%)	19 (38%)	4 (8%)	8 (16%)
History of lead poisoning	0	0	3	3	0	2	0	0	1	3
Highly probable cause for hyperactivity	0	5	3	1	0	0	4	1	0	0
Possible cause for hyperactivity	0	3	3	1	1	0	2	4	1	2
Controls	4 (11%)	23 (62%)	6 (16%)	4 (11%)	0	0	19 (82%)	3 (13%)	1	1

Discussion

Authorities have commented on some erroneous concepts regarding "normal" blood lead levels.[4] A point commonly made is that most studies equate the lowest level diagnostic of clinically manifest lead poisoning with the upper limits of normal. Unfortunately a level not associated with overt clinical evidence of toxicity does not have to be normal. Symptoms may be overlooked for instance in low level toxicity because no one yet knows what to look for. At this point most authorities agree that a blood lead value below 24.5 ug/100 ml is normal and a value above 55 ug/100 ml is abnormal (although not necessarily treated). Our findings suggest that the arguments for considering any lead elevation above 24.5 ug/100 ml as dangerous, should receive serious attention.

A massive single dose of lead can result in death or severe brain damage, and in many cases a large dose of lead ingested over time can also lead to very severe brain damage. It seems reasonable to infer, therefore that raised levels of lead (not necessarily in the toxic range) present over a long period could be responsible for the minimal brain damage that may be present in the hyperactive syndrome. Our finding of raised post-penicillamine urine-lead levels in combination with the higher blood-lead values indicate that many hyperactive children have had increased body-lead stores for a long time. It is conceivable that one consequence of this constant minimal poisonous assault is hyperactivity. If we hold lead exposure responsible for some cases of hyperactivity (an assumption only), we might predict the following:

(1) There would be little difference in lead value between the normal control group and the "highly probable" cause group (i.e. the group with a likely cause for hyperactivity other than lead.)
(2) The "pure" hyperactive group and the "possible" group would both show raised lead levels. The "possible" group differs from the "highly probable" group in the crucial distinction of a convincing other cause for hyperactivity being absent.

These predictions are supported by the results.

All eight hyperactive children who had also a history of lead poisoning had raised blood and urine lead levels at the time of the study. All but one had been treated with chelating agents at least five years previously. This finding indicates that the treatment of these lead-poisoned children may not have been extensive enough and/or that follow-up procedures had been unsuccessful. It may also mean that hyperactivity heretofore thought to be a relatively common consequence of lead poisoning is not necessarily a consequence at all, but a condition that is dependent on continuing elevations of body lead.

Might the lead levels recorded be a consequence of the child's hyperactivity rather than a hyperactivity cause? This interpretation is not supported by the finding that the "highly probable" cause hyperactive group do not show increased blood or urine lead levels. There are, however, too few children in that group to arrive at a definite conclusion.

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UNTERSUCHUNGEN AN 12.000 PATIENTEN ÜBER DEN EINFLUSS DER LUFTVERSCHMUTZUNG UND DES ARBEITSPLATZES AUF DIE HÄUFIGKEIT DER CHRONISCHEN BRONCHITIS

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KURZFASSUNG

Die bisherigen epidemiologischen Untersuchungen über den Einfluss der allgemeinen und der berufsbedingten Luftverschmutzung auf die Häufigkeit chronischer Atemwegserkrankungen wurden meist an Personen durchgeführt, die noch im aktiven Berufsleben stehen. Daher ist dort nur selten mit fortgeschrittenen Krankheitsstadien zu rechnen.

Wir haben aus den Krankengeschichten aller Patienten der Inneren Abteilungen von 5 Krankenhäusern des linksniederrheinischen Steinkohlenbergbaureviers im Kreis Moers aus den Jahren 1971 und 1972 folgende Angaben herausgezogen:

Geschlecht
Krankenkasse (Knappschaft/Nichtknappschaft)
Lebensalter
Hauptdiagnose
Begleitdiagnose: chronische Bronchitis
Silikose
Behandlungsdauer
Wohnort und Strasse mit Hausnummer
entlassen/gestorben

Von den so ausgewerteten 12.084 Patienten wurde die Häufigkeit der Haupt- und Nebendiagnose "chronische Bronchitis" verglichen zwischen

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- *Männern und Frauen*
- *Knappschafts- und Nichtknappschaftsversicherten*
- *Patienten mit verschiedenem Wohnort.*

Dabei wurden zunächst alle Patienten mit Silikose eliminiert und ausserdem auf vergleichbares Lebensalter geachtet. In allen Krankenhäusern war die Haupt- und Nebendiagnose chronische Bronchitis bei den knappschaftsversicherten Männern signifikant häufiger als bei den nichtknappschaftlich versicherten Männern (im Mittel 18,4% : 10,4). Die Häufigkeit bei den Frauen lag niedriger und zeigte in vergleichbaren Altersgruppen keine signifikanten Häufigkeitsunterschiede zwischen den beiden Versicherten gruppen. Dies spricht gegen einen Einfluss des Wohnortes, der bei den Knappschaftsversicherten im Mittel dichter an den Quellen der allgemeinen Luftverschmutzung liegt. Auch für Patienten aus verschiedenen Wohnorten mit underschiedlicher Luftverschmutzung liess sich ein Häufigkeitsunterschied der chronischen Bronchitis nicht statistisch sichern.

ABSTRACT

Up to the present time, epidemiological studies on the effect of general air pollution and of occupational exposure to polluted air on the incidence of chronic diseases of the respiratory tract have mostly been carried out among persons still in active employment. For this reason advanced stages of the diseases are seldom to be expected there.

We extracted the following data, for the years 1971 and 1972, from the medical records of all in-patients in five hospitals in the Moers district of the coal-mining area located left of the lower Rhine:

Sex
Sickness benefit fund (miners' provident fund or other)
Age

Main diagnosis
Secondary diagnosis: chronic bronchitis
Silicosis
Duration of treatment
Postal address
Discharged/died

Among the 12,084 patients investigated, the frequency of chronic bronchitis as the main and secondary condition was compared between:

- men and women,
- miners' provident fund members and other patients,
- patients coming from different localities.

First, all silicosis patients were excluded, and comparability with regard to age was taken into consideration. In all hospitals, chronic bronchitis as the main and as the secondary condition was significantly more frequent among male members of miners' provident funds than among other male patients (average, 18.4% as against 10.4%). The frequency in women was lower, and in comparable age groups showed no significant difference between the two insured groups. This suggests no influence by the place of residence, which in the case of those insured with the miners' provident fund, was usually located closer to the source of the general air pollution. Also, there was no statistical difference with respect to the incidence of chronic bronchitis between patients from different localities exposed to different levels of atmospheric pollution.

Methodik

Es wurden alle Krankengeschichten von denjenigen Patienten ausgewertet, die auch im Einzugsbereich der Krankenhäuser wohnen und zur Behandlung, nicht zur Begutachtung ins Krankenhaus kamen. Da jeder Stationsarzt Patienten beider Versichertengruppen behandelt, ist eine unterschiedliche Diagnostik in beiden Gruppen unwahrscheinlich.
Die knappschaftsversicherten Männer sind zu über 80% Bergleute (gewesen) und somit beruflich staubexponiert, während für die nichtknappschaftlich Versicherten eine berufliche Staubexposition bei der Industriestruktur des Kreises Moers unwahrscheinlich ist. Es gibt keine Hinweise auf unterschiedliche Rauchgewohnheiten zwischen beiden Versichertengruppen.

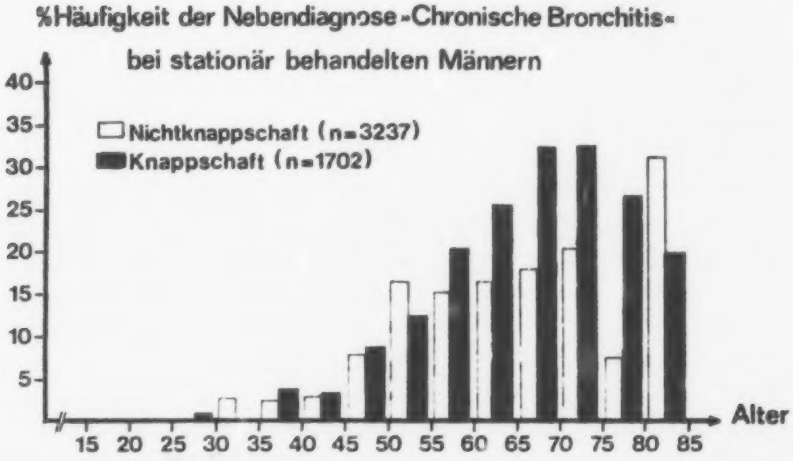
Ergebnisse

Da das Lebensalter der Patienten mit der Diagnose "chronische Bronchitis" in allen Gruppen über 60 Jahre liegt, sei hier die Häufigkeit bei den Fällen ab dem 55. Lebensjahr für die Hauptdiagnose "chron. Bronchitis" gezeigt:

Männer		Frauen	
Knappschaft	Nichtknappschaft	Knappschaft	Nichtknappschaft
10,2%	4,6%	2,2%	1,9%

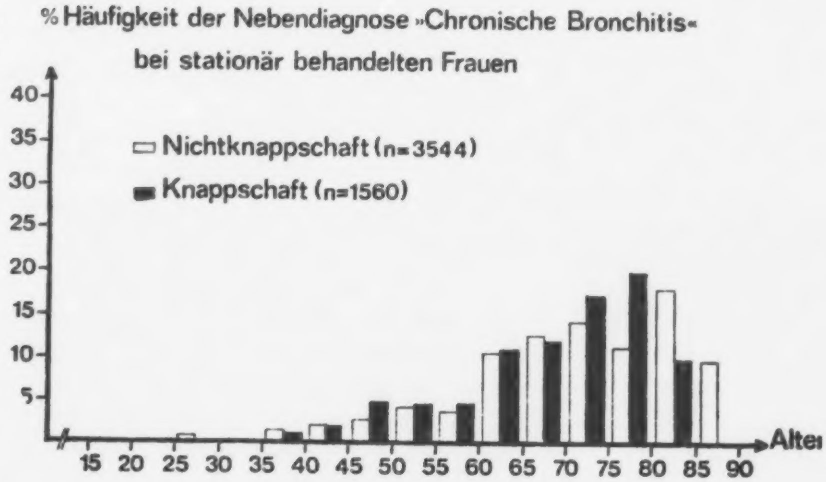
Bei dieser Überhäufigkeit der knappschaftsversicherten Männer könnte man vermuten, daß Bergleute mit einer Bronchitis eher von den Hausärzten zur stationären Behandlung eingewiesen werden als Nichtbergleute, wenngleich diese Unterstellung durch nichts zu belegen ist.
Dieser Verdacht ist aber erst recht unbegründet bei der Nebendiagnose "chronische Bronchitis", deren Häufigkeit in den verschiedenen Altersgruppen in Abb.1 für die Männer und in Abb.2 für die Frauen aufgetragen ist. Hierbei sind alle Fälle außer denen mit der Hauptdiagnose chronische Bronchitis erfaßt, jedoch nur die nicht verstorbenen Patienten, um Fälle mit einer präfinalen Stauungsbronchitis auszuschließen. Die größere Bronchitishäufigkeit der knappschaftsversicherten Männer kommt auch hier eindeutig zum Ausdruck.

Abb. 1



%Häufigkeit der Nebendiagnose »Chronische Bronchitis« bei stationär behandelten Männern

Abb. 2



% Häufigkeit der Nebendiagnose »Chronische Bronchitis« bei stationär behandelten Frauen

Für die Letalität, das Lebensalter und die Behandlungsdauer haben sich in den Mittelwerten keine Unterschiede zwischen Männern und Frauen oder zwischen den beiden Versichertengruppen ergeben.

Diskussion

Bei der Auswertung wurden alle Patienten mit einer Silikose aus dem Vergleich ausgeschaltet, so daß die Silikose nicht die Ursache der größeren Bronchitishäufigkeit bei den Bergleuten gegenüber den Nichtbergleuten sein kann.
Da andrerseits bei den Frauen die beiden Versichertengruppen keine signifikanten Häufigkeitsunterschiede zeigten, ergibt sich auch kein Hinweis auf eine durch den Wohnort bedingte Überhäufigkeit der Bronchitis, jedoch ist keiner der in Betracht kommenden Wohnorte als staubfrei zu bezeichnen.
Die Ursache der größeren Bronchitishäufigkeit bei den knappschaftlich versicherten Männern wird in ihrer beruflichen Staubexposition gesehen, so daß die dadurch bedingten Einflüsse auf die Lunge nicht länger als geringfügig angesehen werden können.
Da sich im Lebensalter, der Behandlungsdauer und der Letalität aber keine Unterschiede ergeben haben, ist zu schließen, daß der Verlauf der Erkrankung von der speziellen Ursache unabhängig ist und eigengesetzlich verläuft.

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ECO-GENETICS: HOST VARIABILITY IN HEALTH EFFECTS OF ENVIRONMENTAL AGENTS

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ABSTRACT

An important variable in assessing the effects of environmental agents upon living things is the genetically determined variation in enzymes, cell surfaces, and immune responses of the host. Such genetic variation may influence spread of agents within the body, specific tissue vulnerability, rate of conversion of agents to active (toxic) forms or metabolism to inactive forms. Therefore, individuals may be at relatively high risk for mutagenic, carcinogenic, teratogenic, or inflammatory effects of common agents for which no statistically significant harm can be detected in overall epidemiological investigations.

Certain inherited human disorders are known to make healthy persons more vulnerable to infectious or physical agents. Individuals deficient in the plasma protein alpha$_1$-antitrypsin are much more susceptible than normals to develop emphysema from chronic cigarette smoking and general environment. Many males of Mediterranean or Negro ancestry are deficient in the enzyme glucose-6-phosphate dehydrogenase (G6PD), determined by a gene on the X chromosome. A long list of oxidizing agents can induce severe hemolytic anemia in those with G6PD deficiency. Well-characterized genetic variation in acetylating and esterolytic enzymes causes severe adverse reactions from anti-tuberculous and muscle-relaxing drugs. Individuals with certain abnormal

hemoglobins or erythrocyte enzyme defects are more susceptible to other drugs and carbon monoxide. Variation in cellular membranes, detected by histocompatibility testing, has been correlated with susceptibility to diseases probably triggered by viruses or by ultraviolet radiation. Variation in enzymes of the DNA repair mechanisms may greatly influence mutagenic effects. Abnormalities in humoral and cellular immunity increase the risk of bacterial and fungal infections, as well as of neoplastic transformation.

Other types of vulnerability result from the action of the host on the agent. The risk of developing cancer of the lung is much higher among people who have the genetic trait of high inducibility of aryl hydrocarbon hydroxylase (an enzyme that forms carcinogenic epoxides from aromatic hydrocarbon compounds in cigarette smoke and other emissions) compared with individuals whose enzyme level is increased very little by such exposure.

One may anticipate practical screening methods to recognize individuals at much higher than "normal" or "acceptable" risk to specific agents in defined occupational or geographic environments.

From the field of pharmacogenetics, striking examples have been recognized of differences in the way different individuals respond to drugs or are affected adversely by such agents. An important variable in assessing the effects of environmental agents upon living things is the genetically-determined variation in enzymes, cell surfaces, and immune responses of the host. Such genetic variation may determine or influence the spread of agents within the body, specific tissue vulnerability, rate of conversion of agents to active (toxic) forms, or rate of metabolism to inactive forms. Thus, individuals may be at relatively high risk for mutagenic, carcinogenic, teratogenic, or inflammatory effects of common agents even when no statistically significant harm can be detected in over-all epidemiological investigations. Several excellent reviews of pharmacogenetics exist [1-4].

1. High vulnerability to direct action of exogenous agents

1.1 Alpha$_1$-anti-trypsin [5].

The serum alpha-globulin fraction is largely comprised of alpha$_1$-anti-trypsin, also termed protease inhibitor. The concentration of this acute phase-reactant serum protein increases under various physiologic and pathologic conditions, such as pregnancy, inflammation, injection of typhoid vaccine, and administration of estrogens. Individuals with the deficient ZZ phenotype are known to be predisposed to early-onset of severe pulmonary emphysema; presumably the role of anti-trypsin activity is important in limiting inflammatory responses. Heterozygotes of MZ phenotype and SZ phenotype probably also have significantly impaired response to inflammation. Approximately 10% of the general population are heterozygotes for variants of anti-trypsin activity. Smoking appears to hasten development of chronic obstructive pulmonary disease in heterozygotes as well as homozygotes for deficient phenotypes. It is likely that these individuals also face higher risks of complications from a whole array of other inhaled agents in the occupational and general environment.

1.2 Glucose-6-phosphate dehydrogenase (G6PD).

This enzyme is essential for the pentose-phosphate shunt pathway, generating energy and reduced pyridine nucleotides (NADPH) to maintain the integrity of red blood cells. In the Negro type of G6PD deficiency the level of G6PD activity is about 15% of normal. This activity is adequate for the red cells, unless an oxidative stress is introduced. Oxidizing drugs or foodstuffs or other agents can provoke a severe breakdown of red blood cells with resultant anemia and hemoglobulinuria. It is important to realize that reticulocytes and young erythrocytes have higher G6PD activity than do older cells, so an assay of G6PD after the old cells have been destroyed will give a spuriously "normal" value for G6PD activity. About 1 in 10 Negro males is G6PD-deficient. In the Caucasian type of G6PD deficiency found among males of Mediterranean ancestry, the level of activity is only 1 to 5% of normal. The list of oxidizing agents which can precipitate hemolysis in these patients is even longer 1 . Oxidizing agents other than drugs can be dangerous for these individuals, including naphthalene in moth balls.

About 1% of people are carriers for an entirely different enzyme deficiency, methemoglobin reductase, rendering them susceptible to cyanosis from some of these same common oxidizing drugs, such as dapsone, chloroquine, and primaquine.

1.3 Heavy-Metal Poisoning[1].

Organic mercury compounds have been responsible for a syndrome of neurologic and psychiatric signs called Minamata disease. In two large outbreaks in Japan, there has been considerable variability in the level of exposure at which individuals developed symptoms. An analogous situation may hold for itai-itai disease, thought to be due to cadmium poisoning.

1.4 Adverse effects of foodstuffs.

Fava beans can precipitate severe hemolysis in certain individuals with the Caucasian type of G6PD deficiency. Migraine can be precipitated by the tyramine in various cheeses or by phenylethylamine in chocolates, presumably due to low levels of monoamine oxidase activity in susceptible individuals (Youdim & Sandler, personal communication). The lactose in milk causes intestinal discomfort and diarrhea in large numbers of people who have lactose intolerance after the age of weaning (75% of Blacks, 90-95% of American Indians and Orientals). Foods high in saturated fats may grossly elevate the serum cholesterol and triglyceride levels in individuals with hereditary hyperlipidemias. Gluten in wheat produces intestinal complications in persons predisposed to celiac sprue. Nodular goiter and thyroid adenomas occur more frequently in non-tasters of PTC (phenylthiocarbamide), presumably since these persons are unable to recognize such goitrogens in the diet. Finally, effects of poorly characterized food additives and of various allergenic substances in the environment must be borne primarily by those genetically predisposed.

1.5 Radiation damage and mutagenesis.

Patients with the rare inherited disorder xeroderma pigmentosum lack activity of a normal DNA repair enzyme. Ordinary exposure to sunlight produces so much ultraviolet-induced damage that multiple cancers develop on the skin. This repair mechanism normally provides a "threshold" below which radiation-induced damage may be corrected. It is likely that variation of this and of related enzyme steps in the repair processes of cells will be found and will be correlated with risks of damage from defined exposures.

1.6 Biological agents in the environment.

It is well known clinically that individuals vary in the likelihood of contracting infectious diseases in the face of common exposure. The integrity of skin, respiratory, urinary, bowel, and other portals of entry is very important, as are the immunological responses to such agents. Defects in humoral or cellular immunity predispose to specific kinds of infections; in fact, the type of organism involved is often a clue to the type of underlying immunological defect. The widespread polymorphism of histocompatibility types, representing antigens on cell surfaces, now appears to be correlated with widely varying risks of developing particular diseases. Of current interest is the finding that HL-A27, an uncommon type, is found in extraordinarily high proportions of patient groups with rheumatoid spondylitis, Reiter's syndrome, and uveitis--three disorders of obscure origin likely involving altered immune response.

2. Differences in rate of conversion of agent to active (toxic) form

The enzyme aryl hydrocarbon hydroxylase (AHH) activates a variety of exogenous hydrocarbon compounds, including many drugs, insecticides, steroids, and chemical carcinogens. AHH catalyzes the initial step in the microsomal oxidation of polycyclic hydrocarbons, forming active epoxides. The great variability in AHH enzyme levels induced by carcinogens applied to human lymphocytes cultured *in vitro* has now been demonstrated to be controlled by a single gene [6]. Since such hydrocarbon carcinogens are present in cigarette smoke, it is likely that high inducers are subjected to much higher levels of epoxides than are low inducers with the same amount of inhaled smoke. The general population falls into three groups: high inducers (9%), intermediate inducers (44%), and low inducers (47%). Shaw and his colleagues have now found that high inducers are enormously over-represented among patients with lung cancer and that low inducers are only rarely found with lung cancer. This finding, if confirmed, should stimulate general testing of smokers, as well as a search for other conversion pathways that may determine differences in susceptibility to other types of carcinogens.

3. Differences in rate of inactivation of toxic agents.

3.1 Pseudocholinesterase deficiency--Suxamethonium sensitivity.

Individuals completely deficient in plasma pseudocholinesterase activity (about 1 in 2000 Caucasians) have prolonged muscular relaxation and cessation of breathing when administered the common muscle relaxant Suxamethonium (succinylcholine) for surgery. An altered enzyme is responsible for this life-threatening risk.

3.2 Acetylator phenotype.

About half of the Caucasian and Black populations are "rapid" and half "slow" acetylators of numerous drugs and other agents in the liver. Only 10% of Orientals are slow acetylators. Slow acetylators accumulate higher concentrations of active drug than do rapid acetylators, thus being susceptible to side effects at dosage levels that do not affect rapid acetylators adversely.

4. Metabolic Interactions of drugs or agents taken together

Chemicals found in man's environment that alter the action of other drugs by stimulating microsomal enzyme activity include halogenated hydrocarbon insecticides, urea herbicides, volatile oils, polycyclic aromatic hydrocarbons, coloring agents, nicotine and other alkaloids, food preservatives, and substances such as safrole, beta-ionone, xanthines, flavones, and organic peroxides that occur in food. Other chemicals inhibit these enzyme systems in the liver, including organophosphorus insecticides, pesticide synergists of the methylene-dioxyphenyl type, carbon tetrachloride, ozone, and carbon monoxide[7].

These examples of genetically-determined variation in susceptibility to drugs and other environmental agents should demonstrate that host variability is a potentially very significant factor both for research investigations of the health effects of particular agents and for concerns about public and corporate responsibility.

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THE EFFECTS OF PARTICULATE AIR POLLUTION ON EXPECTATION OF LIFE

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ABSTRACT

A technique was developed by which the effect of particulate air pollution or expectation of life could be quantified and thus utilized in regional air-pollution planning. The methodology was then applied to a regional air shed in order to demonstrate the loss of human functionality incurred for various emission-control practices.

Expectation of life, broken down by age, race, and sex, and calculated from observed mortality rates, was related to particulate air pollution using regression analysis applied to data collected for the year 1960. The observations for the regression were based upon standard metropolitan statistical areas. Many causal variables were included in the regression analyses, which required compensation in the regression procedure for the nonorthoganality of the causal variables. This compensation procedure increases the confidence of the results and greatly decreases the effect of correlated causal variables on the regression coefficients of the pollution variables.

An adequately documented regional air shed was selected as the test region. Air-pollution concentrations over the region for three proposed sets of air-pollution-control regulations were utilized along with the demographic characteristics of the region to integrate per-capita losses over the age, race, sex, and location variables.

The results of the methodology applied to the test region were used to address several hypotheses. Two conclusions reached were:

(1) Expectation of life is an important parameter to measuring the effect of air pollution on mortality, and has the advantage of being commensurable with economic loss.

(2) The change in expectation of life due to particulate air pollution is quite large. An average loss rate for the test area is approximately 3 days per year per capita.

1.0 Introduction

It has been conceded by the Council on Environmental Quality[1] that the ambient-air-quality standards are based upon an inadequate base of information. While many industries claim the standards are much too strict, the other extreme might also be true. Also, owing to the variability of weather conditions, the existence of any (other than zero) average ambient level of pollution will guarantee that there will occur, at some time, an episode serious enough to cause noticeable increases in morbidity. This implies that there is no "safe" level of pollution, meaning that standards, such as those defined by the EPA, should be set according to socioeconomic trade-offs, rather than through determination of safe levels. The work reported in this study was addressed to these considerations.

2.0 Regression Analysis of Expectation of Life and Particulate Air Pollution

2.1 Data Sources

The expectation of life for members of a population is estimable from the mortality experience of the population. Duffy and Carrol[2] have tabulated the mortality rate for the years 1959-1961 by age group, race, and sex for each standard metropolitan statistical area (SMSA). These mortality data can be used to evaluate expectation of life with techniques proposed by Chiang[3], with a slight modification to account for the averaging of 3 years of mortality data.

Lave and Seskin[4] have utilized socioeconomic, pollution, and climate variables to calculate the effect of air pollution on mortality. These data, representing some 24 potential causal variables defined for each SMSA, were kindly provided by Mr. Seskin.

2.2 Regression Procedure

The 24 causal variables defined were utilized in a multivariate regression analysis to develop the relationship of expectation of life(by age, race, and sex) to particulate concentration. The causal variables were found to be highly correlated with each other. Under this condition, a regression analysis yields estimates of coefficients which are unbiased (accurate), but which have a large variance (imprecise). Thus, it is possible for estimated coefficients to be quite different from the true coefficients.

Hoerl and Kennard[5] have presented a technique called ridge regression which alleviates this problem by the addition of a small value to the diagonal entries of the correlation matrix of the causal variables. With this technique, the estimates of the coefficients have a much smaller variance, while becoming only slightly biased. The application of ridge regression thus improves the likelihood that the coefficient estimates are in the neighborhood of their true values.

It is possible to extend the ridge-regression procedure to include weighting. In this study, the case weights were based upon the variance in the estimates of expectation of life.

Two separate regression models were applied. In the first, expectation of life was related to particulate concentration. In the second, the Naperian logarithm of concentration was used.

3.0 Application of Regression Results

3.1 Test Area

A regional air shed for which demographic and industrial data were known was needed to apply the results of the regression model. The area selected was a fully documented environmental planning region[6] derived from an actual city.

Three sets of emission controls were postulated for the city. In the first, no control equipment was placed on any particulate source (except where particulate recovery was an economic necessity). In the second, extremely good equipment was placed on all industry, and residential heating was converted from coal to natural gas. The third was a repeat of the second, except that the city power plant was left uncontrolled.

3.2 Results

Air-pollution concentrations over the city were estimated for these three cases via a climatic air transport model. The concentrations were then coupled with demographic data and regression results to produce the losses in expectation of life due to particulate concentrations. The change due to emission controls was calculated from the difference between the losses for emission controls to the loss for no emission controls. This change, which represents an increment in expectation of life to be achieved (conceptually) at the end of the life span, was apportioned on a yearly basis by division by the nominal expectation of life.

These calculations were performed for the three emission control sets and the two (linear and log) models of the regression analysis. The results show that the benefits to be achieved by emission controls (over the no-control case) expressed in man-days per capita per year are as follows:

Emission Controls	Linear Model	Logarithmetic Model
Extremely Good	3.08	2.73
Uncontrolled Power Plant	0.46	0.66

It is seen that a good set of emission controls applied over the city would result in an increased life span of about 3 days per capita per year. This increase is essentially an increase in productivity, and thus is commensurable with economic loss.

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ILLNESS DUE TO ENVIRONMENTAL POLLUTANTS IN A PHYSICIAN'S PRACTICE

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ABSTRACT

Practicing physicians are frequently confronted with illness due to environmental pollution, but many lack the diagnostic tools for its recognition. Relatively little information is available to the physician on the clinical aspect of such diseases in contrast to an abundance of literature pertaining to the biochemical and epidemiological approach.

This paper attempts to bridge this gap. Data have been gleaned from acute pollution episodes and from chronic low-grade exposure to environmental pollutants which leads to slowly progressive illness. The patient's history, physical and laboratory findings are correlated with available environmental data and elucidated by brief case reports. The modus operandi of respiratory pollutants is discussed in distinction to systemic airborne poisons which enter the system via the gastrointestinal tract. The target organs of the major environmental pollutants are presented diagramatically and the diagnostic features of illness due to air pollution are tabulated.

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Practicing physicians are frequently confronted with illness due to environmental pollution; however many lack the tools for establishing the diagnosis. In contrast to an abundance of literature pertaining to the biochemical and epidemiological aspect, relatively little information is available on the clinical aspect of environmental diseases. This paper constitutes an attempt to bridge this gap.

In order to recognize an environmental disease, the patient's history, clinical and laboratory findings must be correlated with data gleaned from acute pollution episodes and from long-term, low-grade exposure to environmental pollutants.

History: Data on meteorological conditions of the region in which the patient resides such as the prevailing winds, humidity, rainfall must be incorporated into the history. The topography of the area and the distance of the residence from sources of pollution should be taken into account. The onset of the illness must be correlated with the official report on weather conditions and with information available from monitoring for air pollutants. The presence or absence of symptoms during vacation periods, their intensity outdoors compared with that in enclosed places, the simultaneous onset of identical symptoms among other residents of the neighborhood constitute clues concerning environmental diseases. The effect of smoking on the patient's condition should be explored.

Examination: The physical examination must take into account that many environmental pollutants can enter the system through the gastrointestinal tract and the skin, not necessarily through the respiratory organs and that most environmental diseases exhibit a multiplicity of symptoms. Targets of the most common pollutants are represented in Figure I. In the evaluation of the symptomatology, the patient's personality should also be considered and the possibility of malingery be ruled out.

Laboratory Data: The accompanying table presents some of the major laboratory features encountered in illness due to air pollution. Analysis of hair, urine and blood for suspected contaminants are helpful in determining the degree of exposure to atmospheric pollutants but they are not by themselves sufficient to determine the offending agent. Chemical assays of biopsied material are often of value.

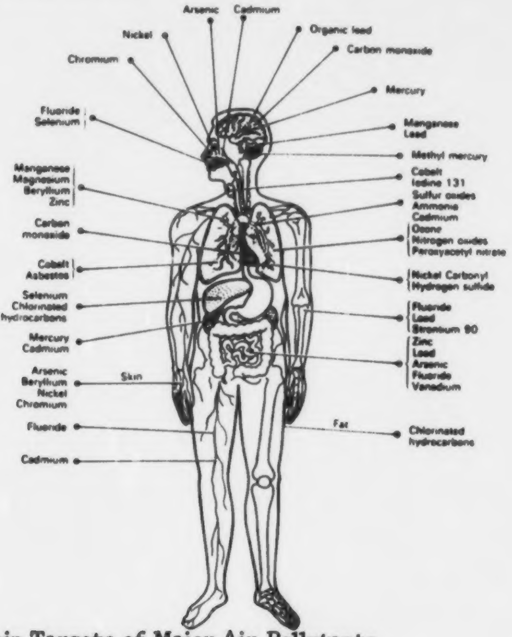

Figure I - Main Targets of Major Air Pollutants

Laboratory Features in Diseases Caused by Major Pollutants

POLLUTANTS	BLOOD	URINE	OTHERS
Arsenic	Arsenic↑ *		Hair, urine (As ↑)
Asbestos			Sputum, ferruginous bodies
Barium	Potassium ↓ *	Potassium↑	
Beryllium	Uric acid↑		Sputum, Schauman bodies
Cadmium	Alkaline phosphatase↑	Microglobulin↑ sulfur↑ Glucose in urine	Nails (Cd ↑)
Carbon monoxide	Carboxyhemoglobin↑		
Cobalt	Cobalt↑		
DDT (chlorinated hydrocarbons)			Fat (DDT ↑)
Fluorides	Alkaline phosphatase↑ Fluoride↑	Fluorides↑	Hair, bones (F ↑)
Hydrogen sulfide	Sulfhemoglobin		
Lead	Red blood cells (stippled) Delta aminolevulinic acid↓	Coproporphyrin III↑, lead↑ Delta aminolevulinic acid↑	X-rays of bones, abdomen
Manganese	Lymphocytes↑		Hair (Mn ↑)
Mercury	Mercury↑ uric acid↑		
Nitrites	Methemoglobin↑		
Organophosphates	Cholinesterase↓	Nitrophenol↑	
Pulmonary irritants			Chest x-ray
Selenium		Selenium↑	
Vanadium	Cholesterol↓ serotonin↑		

* ↑ = increase; ↓ = decrease.

Table I - Laboratory Features in Diseases Caused by Major Pollutants

*From Waldbott, G. L., Health Effects of Environmental Pollutants, The C. V. Mosby Company, St. Louis, 1973.

ASSESSMENT OF THE HEALTH EFFECTS CAUSED BY CHRONIC EXPOSURE TO SOLVENTS

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ABSTRACT

About 120 people living in a small valley in Maryland have been chronically exposed to a mixture of solvent vapors since 1961, when a chemical plant in the valley began operations. A study of the effects of this exposure was begun when many residents, including children, complained of headaches, abdominal pain, and other symptoms. Laboratory tests on these patients showed abnormal glucose tolerance and insulin curves, abnormal lipase levels, and abnormal respiratory function. Liver and pancreatic scans were likewise abnormal. Meanwhile, gas chromatography identified the vapors from at least 25 different solvents in the valley atmosphere or from the water of a creek running through the valley. Nine of these compounds were found in the blood of the patients. Mortality records for the period 1967-74 have revealed an unusually high incidence of cancer among the valley residents, with particular emphasis on malignant lymphoma and pancreatic carcinoma.

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1. INTRODUCTION

For several years, residents of a small valley in Maryland have complained of disagreeable odors in the atmosphere. These odors come from a small chemical plant which began operations in the valley in 1961; the plant recovers solvents from various chemical waste products. No more than 120 people have lived in the valley for at least 2 years during this period. When many of the residents, including children, began showing signs of actual physical distress, we undertook a study of the chemical pollution in the valley and its possible effects on the health of the people. Typical complaints received from the residents were: pain in the upper abdomen, chest, and extremities; pain underneath the ribs, often radiating to the left side and back; burning of the eyes, nose, and throat; headaches, dizziness, fatigue, irritability, and absent mindedness.

2. EVIDENCE OF POLLUTION

Analyses, mainly by gas chromatography, were made of samples of the following: air in the valley, water from a creek running through the plant area, the plant grounds, and blood from residents of the valley. The list of compounds identified in these samples follows; the letters A,W,G and B designate the kind of sample (air, water, ground, and blood) in which the compound was found.

Benzene	A,W,G,B	Acetonitrile	G
Toluene	A,G,B	Acrylonitrile	A,G
Xylenes	G	Acetone	A,W,G,B
Phenol	W,G	Methyl ethyl ketone	A,W,G,B
Nitrophenol	A,G	Methyl i-butyl ketone	A,W,G,B
Nitrochlorobenzenes	A,G	Formaldehyde	A,W,G
Chlorobenzenes	A,G	Methanol	A,W,G
Methyl chloride	A,B	i-Propyl alcohol	A,W,G
Methylene chloride	A,W,G,B	Butanol	A,W,G
Carbon tetrachloride	A,G,B	Amyl alcohol	A,W,G
Trichloroethylene	A,W,G	i-Amyl alcohol	A,W,G
Perchloroethylene	A,G	Furan	G
Tetrachloroethane	A,G,B	Tetrahydrofuran	W,G

Acetic acid	W,G	Ethyl acetate	A,G

These compound were present in mixtures. Several other compounds were detected but not identified.

3. ASSESSMENT OF HEALTH EFFECTS

Statistical analysis of clinical data shows significantly abnormal glucose tolerance and lipase levels in residents of the valley, compared with patients in the hospital. The probabilities of finding these differences by chance were 0.05 and 0.01, respectively. We found that elevated lipase levels, rather than amylase, were the most significant indication of acute pancreatic damage due to exposure to solvents. In addition, residents of the valley showed abnormal insulin curves, usually with a depressed level and delayed peak. None of the pancreatic scans made on ten residents of the valley was completely normal; they generally showed a low count with uneven uptake. Abnormalities were found in liver function studies, ICD levels, PCO_2, and bicarbonate levels. Many of the abnormalities disappeared with removal of the patient from the polluted area. A decreased level of zinc in the blood and/or an increased urinary excretion of zinc were noted.

During the seven year period beginning late in 1967, the death rate in the valley community has been 2,2 times the rate in the County in which the valley is located. The death rate due to cancer has been at least 7 times that in the County. Most of the valley people who died of cancer had lived there for several years, or from birth. Four deaths were due to malignant lymphoma; an increased death rate due to carcinoma of the pancreas was also found. The probabilities that these deaths would have occurred during this period by chance are about 0.00001 for the lymphomas and 0.006 for the pancreatic carcinomas.

4. ACKNOWLEDGMENT

Thanks are due Dr. Elois KAILIN and Dr. N.E. DAY for help in statistical evaluation of the data.

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INCIDENCE DE CERTAINES MALADIES CHEZ LA POPULATION DE DEUX CENTRES FORTEMENT INDUSTRIALISES, COMPARATIVEMENT A TROIS LOCALITES TEMOINS

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RESUME

La morbidité a été étudiée comparativement chez la population de 2 centres dont l'atmosphère est intensivement polluée par des industries diverses, et chez la population de 3 villes témoins dont l'atmosphère urbaine est exempte de pollution intense et spécifique. Les données primaires sur l'incidence des affections ont été extraites des rapports mensuels des circonscriptions médicales. L'étude comprend une période de 7 ans (1963-1969).

La pollution atmosphérique a été considérée comme étant un facteur favorisant de l'incidence de certaines maladies seulement lorsque l'incidence de celles-ci dans le centre industriel dépassait 2,0 fois pour les enfants, ou 2,5 fois pour les adultes l'incidence des mêmes maladies dans les localités témoins.

Les résultats de l'étude montrent que:

Dans un centre à puissante industrie de métalurgie non-ferreuse et chimique, une incidence significativement plus élevée a été constatée pour certaines maladies respiratoires, cardiovasculaires, digestives, neurologiques, psychiques, hématologiques et du métabolisme - chez les adultes; de même pour certaines maladies respiratoires, hématologiques et le rachitisme - chez les enfants (0 - 16 ans).

Dans un centre à industrie de matériaux de construction et chimique, une fréquence accrue a été constatée pour certaines maladies respiratoires, cardiovasculaires et digestives - chez les adultes, aussi bien que pour certaines affections respiratoires et le rachitisme - chez les enfants.

ABSTRACT

The incidence of disease was compared in the population of two centres in which the atmosphere is severely polluted by various industries, and in the population of three control towns free from severe or specific atmsopheric pollution. The primary data on the incidence of the diseases were taken from the area monthly medical reports. The study covers a seven-year period (1963 - 1969).

Atmospheric pollution was considered to be a factor favouring the incidence of certain diseases only when their incidence in the industrial centre was more than twice (in children), or more than 2.5 times (in adults) that of the same disease in the control areas.

The results of the study show that:

In an important centre of the non-ferrous-metal and chemical industries there was a significantly higher incidence of certain respiratory, cardiovascular, digestive, neurological, psychological, haematological and metabolic diseases in adults, and likewise of certain respiratory and haematological diseases and rickets in children in the age range 0 - 16.

In a centre of the building materials and chemical industries there was a greater incidence of certain respiratory, cardiovascular, and digestive diseases in adults, and of certain respiratory conditions and rickets in children.

1. INTRODUCTION

La pollution atmosphérique revêt des aspects différents pour chaque localité, en raison de la nature, de la quantité et du caractère des éliminations nocives, de même qu'en fonction de certaines conditions météorologiques et topographiques locales. Il n'est donc pas dépourvu d'intérêt d'analyser si, dans des localités à diverses industries et intensités de pollution, il existe des différences dans la morbidité de la population. Le but de telles recherches est celui de savoir si la pollution atmosphérique constitue un facteur de risque concernant certaines affections, s'il y a une implication particulière de la pollution dans l'état de santé de la population dans les divers centres industriaux.

Dans le cadre du présent travail la morbidité (l'incidence des cas nouveaux) a été étudiée comparativement chez la population de 2 centres dont l'atmosphère est intensivement polluée par des industries diverses, et chez la population de 3 villes témoins dont l'atmosphère urbaine est exempte de pollution intense et spécifique. Le travail synthétise des données qui ont été en partie publiées (1-5).

2. METHODE

Etant donné l'uniformité de l'organisation de l'assistance médico-sanitaire urbaine, la grande accessibilité (aussi bien au niveau du réseau sanitaire de base, qu'au niveau médical de spécialité), et la standardisation du système d'enregistrement des cas de maladies en Roumanie, on a procédé à l'étude comparative de certaines maladies pour lesquelles il existe dans la littérature des données sur une corrélation possible avec les conditions de la pollution atmosphérique. Notre étude comparative concerne l'incidence des affections respiratoires, cardio-vasculaires, digestives, hématologiques, neurologiques, psychiques, allergiques, de métabolisme et nutrition, les maladies des organes sensoriels, le rachitisme et les tumeurs.

Les rapports mensuels des circonscriptions médicales sur le nombre des cas nouveaux (incidence) de maladies ont servi comme données primaires. On a d'abord fait la somme des cas nouveaux de maladies enregistrées au cours de l'année respective, puis on a rapporté ce nombre à 1000 habitants, adultes ou enfants. L'étude a compris une période de 7 années (1963-1969). Afin de minimaliser les différences annuelles, on a calculé les moyennes des fréquences annuelles des maladies sur la période analysée.

La moyenne de l'incidence des maladies a été calculée de manière analogue pour les 3 localités témoins, cette incidence étant considérée égale à l'unité (incidence conventionnelle = 1,0).

La pollution atmosphérique a été considérée comme étant un facteur favorisant de l'incidence de certaines maladies seulement lorsque l'incidence de celles-ci dans le centre industriel dépassait 2,0 fois pour les enfants, ou 2,5 fois pour les adultes l'incidence des mêmes maladies dans les localités témoins (incidence conventionnelle plus de 2,0 ou 2,5).

3. RESULTATS

3.1. Dans un centre à une puissante industrie de métallurgie non-ferreuse et chimique, une incidence significativement plus élevée a été constatée pour les maladies suivantes:

Chez les adultes - du groupe des affections respiratoires, la bronchite chronique; le groupe des affections cardiovasculaires (parmi celles-ci, hypertension artérielle, artériopathie coronaire chronique et maladies des artères); du groupe des affections digestives, ulcère gastrique et duodénal; le groupe des maladies du sang et des organes hématopoïétiques (parmi celles-ci, les anémies); le groupe des affections psychiques (parmi celles-ci psychoses, psychonévroses et troubles de caractère et de comportement); les maladies chroniques du système nerveux central; groupe des affections allergiques, endocriniennes, de métabolisme et de nutrition (parmi celles-ci, le diabète sucré).

Chez les enfants - le groupe des affections respiratoires (parmi celles-ci, les infections aïgues des voies respiratoires supérieures, la grippe, la bronchite aïgue et la bronchite chronique); le rachitisme; les maladies du sang et des organes hématopoïétiques (parmi celles-ci, les anémies); les affections psychiques (parmi celles-ci, les psychonévroses, les troubles de caractère et de comportement); les maladies des yeux; le groupe des affections allergiques, de métabolisme et de nutrition.

3.2. Dans un centre à industrie de matériaux de construction et chimique, une fréquence accrue a été constatée pour les maladies suivantes:

Chez les adultes - du groupe des maladies des voies respiratoires, la pneumonie et la bronchite chronique; le groupe des maladies cardiovasculaires (parmi celles-ci, le rhumatisme cardio-articulaire aigu, l'artériopathie coronaire chronique, l'hypertension artérielle); du groupe des affections digestives, l'ulcère gastro-duodénal.

Chez les enfants - le groupe des affections de l'appareil respiratoire (parmi celles-ci, la pneumonie, la bronchite aigue, la bronchite chronique, les hypertrophies des amygdales, les végétations adénoïdes); du groupe des affections cardiovasculaires, le rhumatisme cardio-articulaire aigu.

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BONE MARROW CHANGES IN ASBESTOSIS

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ABSTRACT

Seventeen workers from an Egyptian asbestos-cement pipe factory exposed to asbestos dust, and seldom exposed to silica and cement dust for a period of 10 - 26 years of age range from 30 - 57 years were examined clinically, radiologically, and hematologically including bone marrow puncture.

The result showed a state of leucopenia, increased sedimentation rate, the bone marrow showed a marked to extreme degree of generalized hyperplasia, the outstanding feature is the marked increase in the number of reticulum cells, some of them are immature and binucleated.

These results are discussed in the text.

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INTRODUCTION

The inhalation of asbestos dust produces chronic interstitial pulmonary fibrosis, pleural reaction and might predispose to bronchogenic carcinoma or pleural mesothelioma.

Recent studies on the serum of asbestos workers showed the presence of hyperproteinemia, hypoalbuminemia and hypergammaglobulinemia [1], in addition to marked changes in Igs. A, M, and G [2]. T. Warwick [3] (1970), reported an increase in A.N.F. and rheumatoid factors but not a significant increase in antibodies to cytoplasmic constituents.

Similarly rheumatoid factor has been reported in asbestosis by Pernis et al [4] and in silicosis by Vigliani and Pernis [5].

It is likely that several different mechanisms for production of rheumatoid factor will be found.

Disturbance of protein and amino acids metabolism in asbestosis [6], as well as hypoglycemia [7], in addition to hypocholesterolemia and disturbed lipid electrophoresis in the same disease were recently reported [8].

In disorders associated with pronounced hyperglobulinemia, there is an increase of plasma cells [9].

El- Waraaki et al [10], examined the bone marrow specimens of 7 workers having silicosis. The pattern of changes noted was in the form of generalised hyperplasia, and in particular there were very high figures for the myeloid series, reticulum cells and plasma cells. The eosinophils showed a slight but definite increase, but the erythrocytes, megakaryocytes, lymphocytes and monocytes were within normal limits.

These changes were considered to be related to silicosis since other diseases causing stimulation of the bone marrow had been adequately excluded.

Bone marrow has not received universal attention in workers exposed to asbestos dust.

The evidence presented in favour of an auto- immunological mechanism operating in asbestosis stimulated this study of bone marrow in workers exposed to asbestos and showing various graded of radiological shadows.

Therefore the purpose was to investigate these anticipated changes and to clarify their significance in the diagnosis and prognosis of asbestosis.

MATERIAL AND METHODS

Seventeen workers from an Egyptian asbestos - cement pipe factory exposed to asbestos dust (crocidolite, chrysotile and amosite) [11], and seldom exposed to silica and cement dust, for a period of 10 to 26 years and of age range from 30 to 57 years were the subject of this study.

These workers were admitted to N.H.S. Helwan hospital. They were examined clinically. Clinical examinations of all cases revealed no enlargement of the liver, spleen, or lymph nodes, no abdominal masses were felt. Sputum analysis was repeatedly negative for acid fast bacilli by direct smear examination. The sputum was also examined for malignant cells by staining with Papanicolau stain [12] no malignancy was detected. Large chest radiographs were done and the cases were classified according to the extent of radiological findings.

A single bone marrow puncture was performed in each case. Serological tests for syphilis, salmonella, and brucellosis were free. The patients were afebrile throughout the time they spent in hospital and they had no skin lesions or itching. A special search for parasites in urine, stool, blood and bone marrow specimens was done, but all were negative.

Blood samples were collected and examined for:

I - Total and differential white blood cell count
II - Hemoglobin %, R.B.Cs. count and reticulocytes
III - Platelet count, haematocrite value and sedementation rate

Bone marrow was examined for: Total and differential count.

RESULT

I BLOOD CHANGES

Table I shows the findings in blood, in this table we notice a state of leucopenia in almost all cases ranging from 3000 - 5.600, a slight but persistent eosinophilia 5 - 20%, the hemoglobin % was within normal limits 12.5 - 16 gms. %. Reticulocytes, hematocrite and platelets count were within the normal range.

TABLE I (Blood Picture Changes in Asbestosis)

Name	Age	Period of exposure	Extent of X-ray	Physical signs	Hb. % gm. %	R.B.Cs.	T.L.C. in 1000	B. E. St.	Sq. L. M.	Platelet in 1000	Retic %	Sed. Rate
K.M.+	40	26	+	+	14	48	3.8	0 8 6	42 36 8	200	1	9/20
M.H.+	50	22	+	++	14	5	5.4	0 6 2	56 34 2	280	1	30/70
M.M.+	50	13	+	+	13.5	4.8	4.2	0 10 4	54 30 2	200	0.3	19/40
A.A.+	57	26	++++	+++	13	4.7	3.8	0 14 4	60 18 4	250	0.5	16/30
S.I.+	49	25	+	++	13	4.5	3.8	0 6 6	48 32 8	300	1	14/30
A.A.+	52	20	+++	++	13	4.7	4.2	0 20 0	20 52 8	300	0.5	18/40
M.D.+	51	22	+++	+++	12	4.0	3.2	0 9 2	51 32 5	200	0.4	40/80
M.I.+	35	20	++	+++	12	4.0	3.9	0 16 2	38 36 8	150	2	20/40
E.F.+	49	21	++	++	13	4.9	4.9	0 10 6	60 22 2	230	0.8	8/20
M.E.+	32	13	+++	++	14	4.7	3.4	0 12 2	54 26 6	350	1	30/60
A.A.	40	10	+++	+	14	5.2	4.6	0 6 6	52 36 0	250	0.8	22/45
S.Z.	49	11	-	-	13	4.7	4.6	0 5 3	66 20 6	380	0.7	11/24
G.H.+	40	22	++	++	14.5	4.8	5.6	0 6 4	58 22 10	245	0.6	3/5
F.L.+	33	16	++	++	13	4.4	3.4	1 8 4	20 58 8	250	0.3	20/40
A.S.+	49	10	+	+	14	4.7	4.0	0 6 10	68 14 0	200	0.2	12/26
S.M.	49	11	+	+	16	5.1	3.8	2 14 6	34 38 6	286	0.2	8/17
A.R.+	40	23	++++	++++	13	4.4	3.0	0 12 4	42 34 8	280	0.6	40/80

+ on top of initials means that they are repeated in the 2 tables.

+ to ++++ = the degree of severity of either the x-ray or the physical signs and symptoms.
Figure 3,4 and 5 are examples for the severity of the x-ray.

Sedimentation rate using the Westergreen method was in almost all cases higher than normal.

Bone marrow showed a marked to extreme degree of generalised hyperplasia.

The myeloid series showed a marked hyperplasia of its elements. There is a definite increase in the number of eosinophils. The erythroid series showed a normal process of maturation of its elements which are present in normal numbers. The megakaryocytes are present in normal numbers and showed a normal process of platelet separation. The lymphocytes and monocytes are present in fairly normal numbers and showed no morphological anomalies.

There is an increase in the number of plasma cells some are immature and binucleated (table II), figure 1.

The outstanding feature is the marked increase in the number of reticulum cells, some are binucleated similar in morphology to Dorothy Reed cells, Figure 2.

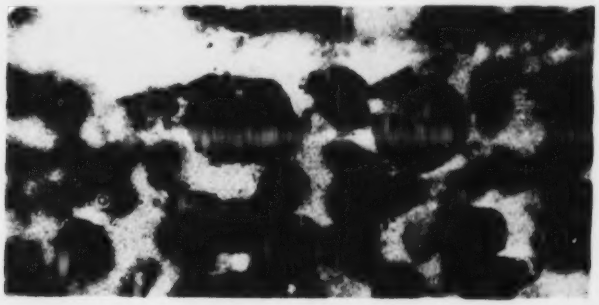

Figure 1.: Immature and Binucleated plasma cells

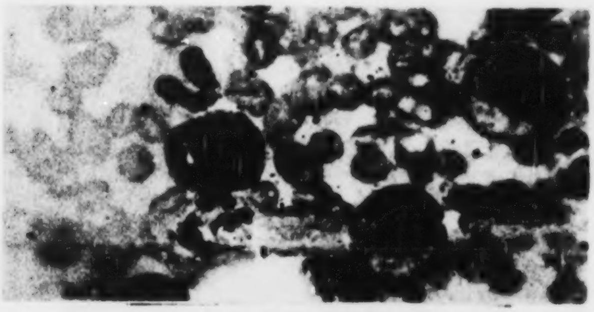

Figure 2.: Binucleated reticulum cells

TABLE II (Bone Marrow Changes in Asbestosis)

Name	T.C. in 1000	MYELOID SERIES % B E BL.	PRO.	MYE.	JUV.	ST	SO.	LYMPHORETICULAR SERIES. RC.	PP.	L.	M	ERYTHROID	MEGAKARYOCYTE	COMMENT
K.M	320	0 4 2	5	10	9	9	15	2	5	14	0	24	Normal	normoblastic reaction, giant binucleated cells
M.H.	165	0 7 0	1	18	11	15	15	2	6	8	0	15	Normal	Giant binucl. cells
M.M.	320	0 5 2	2	18	15	17	15	3	1	10	0	12	Normal	Giant binucl. cells
A.A.	200	0 9 0	0	9	13	17	20	3	5	10	0	14	Normal	Giant binucl. cells
S.I.	320	0 8 0	3	13	14	25	14	3	3	7	0	10	Normal	Giant binucl. cells
A.A.	164	0 15 0	1	11	6	21	17	2	5	7	1	17	Normal	Giant binucl. cells & increased mitosis
M.D.	265	0 9 2	0	11	10	10	15	3	5	11	2	22	Normal	Giant megaloblastic changes & giant binucleated cells
M.I.	320	0 15 1	0	15	10	17	6	2	6	17	2	14	Normal	Increased macrophages & histiocytes
E.F	210	0 8 0	1	10	11	20	13	4	6	7	1	19	Normal	Giant binucl. cells
M.E.	240	0 9 0	1	13	15	20	13	4	6	23	3	6	Normal	N.A.D.
G.H.	200	1 7 0	0	12	7	25	12	3	4	15	2	12	Normal	Immature plasma & giant binucl.cells
F.L	95	0 9 1	0	9	9	21	14	0	3	6	2	26	Normal	Giant binucl. cells
A.S.	198	0 4 0	0	12	12	26	11	2	5	6	1	21	Normal	Many binucl . plasma & giant cells
A.R.	286	0 6 0	0	5	4	21	15	2	6	20	10	21	Normal	Many immature plasma cells
S.M.	280	0 2 0	1	18	5	16	24	2	3	12	1	16	Normal	Increased mitosis, giant binucl. plasma & giant cell
A.M.	360	0 11 1	1	15	7	22	17	2	5	1	1	22	Normal	Giant binucl. cells & megalobl. changes

normal range (50.000 to 100.000) see reference 10 for comparison with normal
T.C. - total count, B = basophil; E = eosinophil; BL. = blast, PRO = promyelocye, MYE = myelocyte, ST = stratified cells
SO. = squames, juv. = juvenile, RC = reticulum cells, PP = plasma cells, L. = lymphocytes, M. = monocytes.

Figure 3.

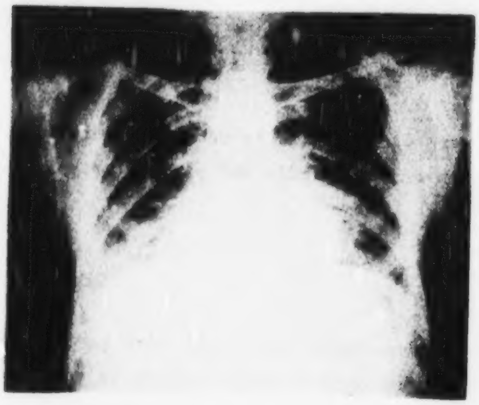

Figure 4.

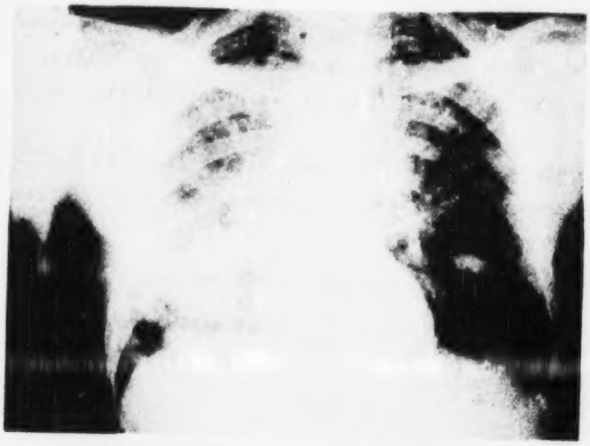

Figure 5.

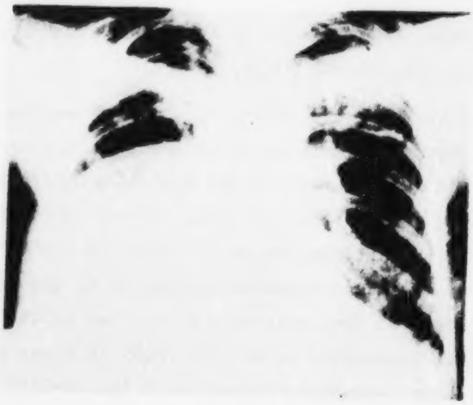

Figure 3, 4, 5 : Examples of the Severity of Lung Damage.

The total count of the nucleated cellular elements of the marrows examined varied between 95.000 and $360.000/mm^3$. (normal marrow 50.000 - 100.000).

These changes were very similar to changes observed in the bone marrow in certain forms of reticulosis and particularly in association with malignant lymphoma.

DISCUSSION

It is pertinent to emphasize that these bone marrow and blood changes were related to the inhaled dust produced in this industry (asbestos, silica and cement), thorough clinical examination and laboratory investigations were carried out to exclude other diseases that may stimulate the bone marrow i.e. specific fevers, syphilis, leukemia, Hogkins' disease, Bilharziasis, malaria and other tropical or skin diseases.

From the above results it is evident that the bone marrow picture was definitely abnormal in the cases of asbestosis and/or mixed dust pneumoconiosis investigated.

These changes observed showed the following:

1 - Generalised hyperplasia in almost all cases with particularly high figures for the myeloid series, reticulum cells and plasma cells

2 - A slight but definite increase in eosinophils

3 - Erythrocytes, megakaryocytes, lymphocytes and monocytes were within the normal range.

It is appreciated that if lesions of the bone marrow are focal in distribution, the puncture as well as the trephine biopsies cannot be representative of the overall state of marrow activity. The fact, however that all cases showed more or less the same abnormal results may be taken as evidence of the diffuse nature of these abnormalities.

There was no correlation between the degree of the bone marrow reaction and the extent of the radiological shadows in the lungs. On the other hand, the total leucocytic count was found in these cases to be on the low normal level or leucopenic in spite of the myeloid hyperplasia of the bone marrow, this might be explained on the assumption that leucocytes are mainly phagocytosed in the reticulo-endothelial tissue of the lungs, and this is assumed to take place in asbestosis and mixed dust pneumoconiosis as El- Warraki et al [10] found similar findings in silicosis.

In conclusion the similarity of these findings to silicosis in addition to the presence of binucleated reticulum cells and the hyperplasia of the bone marrow as in cases of reticulosis and lymphomas stimulates further research on the aetiopathogenesis of pneumoconiosis.

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BEHAVIOUR OF RATS AND THE THRESHOLD LIMIT VALUE OF TRICHLOROETHYLENE

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ABSTRACT

Objective evidence concerning health effects of low doses of a solvent like trichloroethylene (TCE) will probably continue to come largely from tests of animal behaviour, because its main toxic action is on the central nervous system and because the long-term, low-dose evidence from man may be considered subjective.

Groups of 16 male rats were exposed singly to TCE vapour at 100ppm (535mg TCE/m^3*), or 200, 500 or 1000ppm 5 x 6 hours a week for about 5 weeks (12 weeks at 100ppm). Social behaviour was observed, usually once a week, in the 5 min. immediately following exposure. Control rats show their highest spontaneous activity on return to the home cage after daily separation, and TCE reduced this activity. In a social situation, activity is of several kinds but, unlike most centrally-active drugs, the reduction due to TCE was fairly uniform with little evidence of stimulation or depression of any one kind of behaviour.*

The fall in activity due to TCE was significant after 1 day at 1000ppm. Following 100ppm, activity fell after 1 day in one group of rats, but after 1½weeks in another and as much as 8½ weeks in a third.

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In a test of exploration and learning in an unfamiliar cage, thirsty rats exposed to TCE were quicker than controls to find water and begin drinking. The rate of exploratory movement was unaffected.

The present threshold limit value for TCE in Britain is therefore not a no-effect level. Tentative interpretations of the effects are:

(1) that a fall in the highest rate of spontaneous activity is consistent with the drowsiness and fatigue complained of by exposed humans, and

(2) that a low dose of an anaesthetic might well be expected to lead to a slight loss of inhibitory control in an unfamiliar situation.

1. Introduction

1.1. Some effects of environmental pollutants seem to be considered negligible, for in practice far more action is taken on some effects than on others, and a theoretical distinction is implied by the American Conference definition of a threshold limit value (TLV) in terms of "conditions.....without adverse effects" (our emphasis). Before it is safe to distinguish the trivial from the harmful, we need to know as much as possible about a) the dose and duration of exposure which produces any detectable effect, and b) what kind of effect it is. Though obvious, this is easier said than done.

1.2. A particular problem concerns TLVs for the vapour of solvents like trichloroethylene (TCE). In the U.K. this is at present 100 ppm. At high concentrations, TCE is a useful anaesthetic/analgesic, while CNS-related symptoms are also reported in surveys of people occupationally exposed to low concentrations. However, while symptoms like drowsiness, fatigue, headache and gastro-intestinal disturbances are often not trivial, they are not altogether reliable because they depend on self-report and because they occur frequently in control populations. Formal psychophysiological tests are useful, provided the available methods are relevant to the postulated effects, but TCE has cumulative effects which make it difficult to achieve sufficiently long exposure in controlled experiments or adequate control data in people chronically exposed at work.

1.3. Basic objective evidence on TCE at concentrations near the TLV is therefore likely to come from suitable experiments on animal behaviour. The proviso is that methods are selected which will be sensitive to a variety of possible effects and yet which will discriminate between them, and which will also be statistically reliable. Moreover it should be possible to relate the results to any available information from man. Published evidence from animals varies considerably in value on these criteria, and we report here an attempt to supplement this evidence.

2. Behaviour of rats exposed to TCE vapour

2.1. Methods Groups of 16 male albino rats were housed in pairs but exposed singly for 6 - 7 hours daily, 5 days a week to TCE at 100, 200, 500 or 1000 ppm. Vapour was generated by syringe and atomiser into a metered stream of clean air. Each TCE group was matched with controls separated daily into small holding cages, and a dummy experiment compared such controls with a group in the exposure chambers breathing clean air.

Social behaviour was observed as described by Silverman (1971). Paired rats which are separated daily and returned to their home cage early in the dark phase of a 12 hour white/dim red lighting cycle, show a very high rate of spontaneous activity for a few minutes. On the ethological assumption that behaviour is composed of recognizable elements, the acts and postures described by Grant & Mackintosh (1963) were observed for 5 minutes. These occur in functional groups which are differentially sensitive to drugs. For example chlorpromazine reduces the total activity, but within this, disproportionately reduces all forms of social approach while increasing escape away from another rat, without altering exploration, eating or grooming. A low dose of nicotine selectively reduces aggression, thus one kind of behaviour acts as an internal control for drug effects on another (Silverman 1966, 1971).

Social behaviour was observed in a baseline for each experiment, again after one day's exposure to TCE, then usually after three days and weekly for five weeks, in one experiment at 100 ppm for twelve weeks. Controls then received a "crossover baseline" observation in the exposure chambers and one day's exposure to TCE.

An "exploration-thirst" test combined a measure of motor activity with a simple learning task. On two successive days after overnight deprivation of water, rats were placed singly for five minutesin an unfamiliar plastic cage similar to their home cages. Exploratory movements (expressed as movements/minute) were recorded whenever the rat paused to sniff at floor, wall or roof. The latency before the rat found and began to drink from a water bottle was also recorded (as the square root of the time in sec), separately if necessary for the first brief drink and the first of longer than 10 sec.

2.2. Results

2.2.1. Social behaviour. The main finding was a consistent reduction in the sum of elements of all kinds observed in 5 minutes (the "total activity"). A dummy experiment showed that any fall in activity due to the exposure chambers themselves was transient. Analyses of variance ($P < .05$ at 1 and 3 days, $P < .001$ from 10 to 38 days and in X1) followed by t tests showed (see fig. 1) that although exposed rats could not be distinguished by gross observation, a) a concentration of 1000 ppm significantly reduced activity after one day's exposure b) at 100 ppm there was a similar fall, but only after repeated exposures. One group of rats, moderately active at first, showed a significant reduction after 1½ weeks exposure; another group, highly active, showed a fall only after two months. These also showed a post-exposure rebound, by comparison with which their matched controls reduced activity after one day's exposure.

The reduction in activity was fairly uniform among different kinds of behaviour (by multivariate analysis of variance). Reductions specifically in exploration of the cage and submission to or escape from the other rat occasionally reached the 5% significance level.

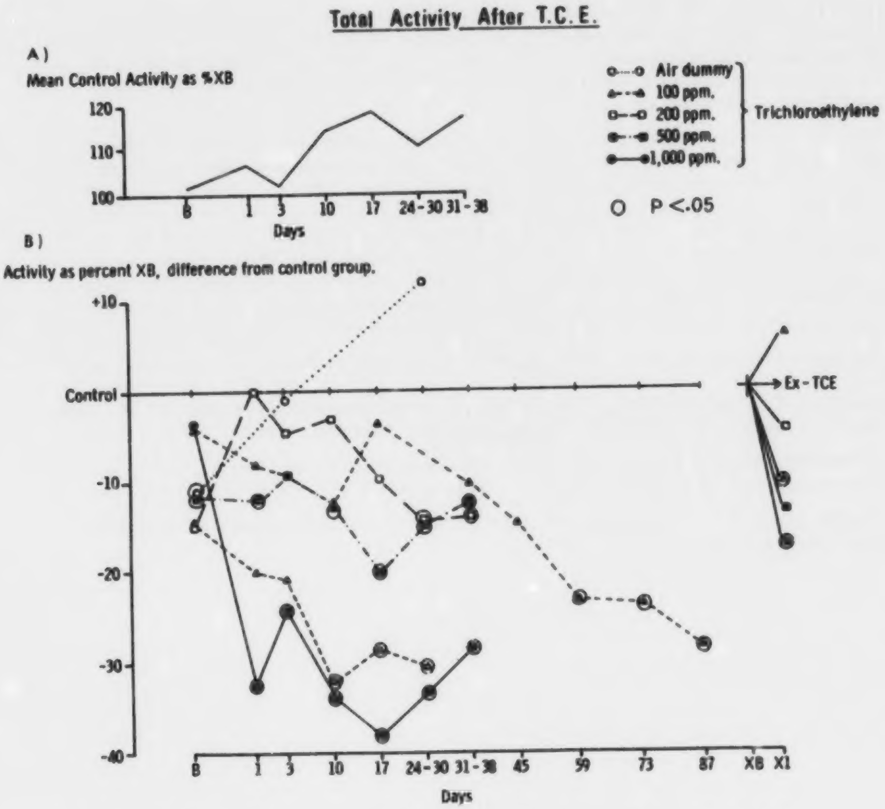
2.2.2. In the exploration-thirst test after 2½ or 5 weeks exposure, TCE caused rats to begin both the first brief drink or the first of more than 10 sec sooner than controls. Exploratory motor activity was unchanged, averaging 13.70 movements/min for TCE-exposed rats on trial 1 against 13.40 for controls, and 15.80 against 15.68 on trial 2. Exposed rats never took longer than controls to begin drinking, and were significantly earlier in trial 1 at 200 ppm and trial 2 at 100 and 1000 ppm. Within the five minute observations exposed rats did not drink for longer than controls.

3. Discussion

3.1. There was an interesting interaction between the concentration of TCE, the duration of exposure, and "individual" differences between batches of rats. The highest concentration of TCE tested reduced total activity after a single day's exposure, the lowest did so only after repeated exposures and one batch of rats was much more susceptible than another.

3.2. Any gross neuromuscular disturbance would have been visible under the close observation, and a motivational disturbance would have been detected as a specific change in the appropriate behavioural category. The absence of such findings and the moderate decline in activity, makes the results consistent with subjective reports in man:- reduced activity when controls' activity is maximal could be secondary to the rats' equivalent of drowsiness, fatigue or headache in a familiar situation.

3.3. In the exploration-thirst test, TCE allowed thirsty rats to begin drinking sooner than controls, yet they were equally likely to interrupt



Total Activity After T.C.E.

Fig 1. Total activity in the baseline (B) observation of social behaviour and after exposure to TCE 6 - 7 hours a day, 5 days a week.

A) Mean activity of the control groups expressed as a percentage of their activity in the crossover baseline (XB) observation.

B) Activity of rats from the exposure chambers in the baseline observation and after exposure to TCE. Difference from controls in activity as % XB.

Former controls breathed clean air in the exposure chambers (XB) and were then exposed for 1 day to TCE (X1).

Circled points show reductions significant at P< 0.05 by t test after analysis of variance of the untransformed activity scores.

drinking for a littlefurther exploration before drinking continuously for 10 sec. Although TCE had none of the paradoxical motor-stimulant effects of low doses of barbiturates, TCE could well have increased responsiveness to stimuli or reduced anxiety in an unfamiliar situation as these drugs have been suggested to do.

3.4. In rats therefore, the TLV for trichloroethylene in the UK and elsewhere (100 ppm) is not a no-effect level, if methods are used which minimise the inevitable laboratory restrictions on the animals' flexibility of response. Extrapolating the present results to man, we would expect TCE to reduce the rate of working on a familiar self-paced task. Some individuals would be more sensitive than others, but there might be a trade-off between concentration and a sufficiently continuous exposure. In unfamiliar (emergency ?) conditions, exposed people may respond sooner; this could be beneficial but could also represent a lack of proper caution.

The experimental work in this paper has been submitted for publication.

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MUTAGENITÄTS - VORTESTE AUF CARCINOGENE WIRKUNGEN VON UMWELTCHEMIKALIEN

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ABSTRACT

(1) From the mutational processes induced by environmental agents usually the numerical and structural chromosome aberrations as well as different types of molecular mutations on the DNA-level are observed. Until now only in microorganisms clearly defined molecular mutations can be demonstrated.

(2) According to recent opinions, at the beginning of carcinogenesis mutational changes of the DNA take place. In spite of former difficulties a correlation exists between mutagenic and carcinogenic actions of chemicals. For these reasons it is possible to develop a pattern of mutation tests, which can serve as a prescreening method for carcinogenic effects:
a) Direct action of the substance to be tested on strains of Saccharomyces cerevisiae (eukaryotic cells, genetically well analyzed, in stable haploid or diploid strains), which show induced suppressor mutations or induced gene conversions.
b) Treatment of mammals and examination of the bone marrow (or blood cultures) for chromosome aberrations. c) Injection of yeasts in the ventral cavity or in the urine of treated animals and test for induced mutations or recombinations. d) In vitro test with liver microsomes and yeasts to cover the effect of short-lived metabolites. e) Treatment of yeasts with synthesized metabolites, which are known to arise in the organism treated.

(3) The usefulness of the genetic prescreening method has been shown with two carcinogenic compounds: Cyclophosphamide and Benzo(a)pyrene. The advantages of the method consist in a short duration of the tests, small amounts of substances used and the possibility of testing a great number of compounds and their combinations.

Im Gegensatz zu den akuten Wirkungen von Umweltagentien auf die menschliche Gesundheit werden die sogenannten Spätschädigungen weniger beachtet. Ihre Wirkungen treten erst nach einem stummen Intervall auf: Die Änderungen des Erbgutes (Mutationen) als erster Typ wird in einer der Folgegenerationen nach der Einwirkung sichtbar; die induzierte krebsige Entartung als zweiter Spätschädigungstyp nach Jahrzehnten.

Bei der großen Zahl von Umweltchemikalien, die noch nicht auf carcinogene Wirkung untersucht sind, sowie bei der Dauer und Kostspieligkeit derartiger Experimente ist es zweckmäßig, einen Vortest auf mögliche carcinogene Wirkungen einer Substanz zu entwickeln.

Nach neueren experimentellen Ergebnissen sind bei der krebsigen Entartung der Zellen mutative Änderungen an der DNS entscheidend beteiligt und es besteht eine gute Korrelation zwischen mutagener und carcinogener Wirkung einer Substanz. Es ist daher möglich, aus der großen Zahl von Mutagenitäts-Prüfverfahren ein Vortest-Muster zusammenzustellen, das einen optimalen Schluß von der induzierten Mutabilität auf eine carcinogene Wirkung zuläßt. Im Gegensatz zu den typischen Mutagenitätsprüfungen dürfen hier nur Teste an somatischen und nicht an Keimzellen verwendet werden.

In der Tabelle I sind die aufeinanderfolgenden Prüfverfahren des Carcinogenitäts-Vortestes zusammengestellt. Nachgewiesen werden in Knochenmark oder Blutzellen von Säugetieren (Chinesischer Hamster) induzierte numerische oder strukturelle Chromosomen-Aberrationen. Mit Stämmen von Saccheromyces cerevisiae (Hefe) werden als definierter Mutationstyp die Suppressormutationen im Isoleucin-Valin-lGenlocus sowie als Rekombinationstyp die mitotischen Genkonversionen in zwei Genloci erfasst. Beide DNS-Änderungen sind streng miteinander korreliert (1), sodaß in der Regel die Bestimmung der Genkonversion als das empfindlichere System genügt.

Die Veränderungen der zu prüfenden Substanz im Metabolismus des Säugers wird durch Injektion der Hefezellen in die Bauchhöhle, durch Exposition mit Harn behandelter Tiere sowie

Tabelle I: **Mutagenitäts-Vorteste auf carcinogene Wirkung mit Cyclophosphamid und Benzo(a)pyren**

Objekt	Technik	Mutationstyp	Cyclophosphamid	Benzo(a)-pyren
Saccharomyces cerevisiae	Direkt-Behandlung	Mitotische Genkonversion	-	-
Behandeltes Säugetier (Chines. Hamster)	Knochenmark (Blutkultur)	numerische und strukturelle Chromosomen-Aberrationen	+ 1)	+
	Injektion Bauchhöhle: Saccharomyces	Mitotische Genkonversion	(+)	-
	Urin: nach Behandlungsbeginn Saccharomyces	Mitotische Genkonversion	+	-
Saccharomyces cerevisiae	In vitro: Lebermikrosomen + Saccharomyces + Substanz	Mitotische Genkonversion	+	+ 1)
	Direkt behandelt + synthetisiertem ultimalen Carcinogen	Mitotische Genkonversion	n.t.	+ 1) (Epoxyd)

1) Ergebnisse aus der Literatur

n.t. = nicht geprüft

durch den in vitro Versuch mit Lebermikrosomen und zu prüfender Substanz einbezogen. Dieser Test wird durchgeführt, um auch kurzlebige aktive Metabolite nachweisen zu können. Sofern die aus den verabreichten Substanzen im Metabolismus entstehenden ultimalen Carcinogene bekannt und synthetisiert sind, werden sie durch direkte Einwirkung auf Hefezellen oder Blutkulturen getestet.

Die Brauchbarkeit dieses Vortest-Musters ist mit zwei carcinogenen Substanzen geprüft worden: Cyclophosphamid als alkylierende, bei direkter Wirkung auf Mikroorganismen scheinbar nicht mutagene Substanz sowie Benzo(a)pyren als carcinogener, aromatischer Kohlenwasserstoff, der als Beispiel für die Nicht-Korrelation von Mutagenität und Carcinogenität häufig herangezogen wurde.

Cyclophosphamid löst zahlreiche Chromosomen Aberrationen aus; seine genetisch aktiven Metabolite sind im Urin in über 100 facher Konzentration als in der Lymphe vorhanden und nachzuweisen (2), desgleichen im Lebermikrosomen-Test (Siebert unveröff.). Benzo(a)pyren löst bei höherer akuter Dosierung Chromosomenaberrationen aus, seine aktiven Metabolite sind nur im Lebermikrosomentest nachzuweisen, desgleichen bei direkter Wirkung der synthetisierten ultimalen Carcinogene (Epoxyde der K-Region. 3).

Diese vorläufigen Ergebnisse mit zwei genetisch besonders schwierigen Substanzen lassen das ausgewählte Muster von Vortesten geeignet erscheinen, im Falle positiver Ergebnisse auch eine carcinogene Wirkung der Substanz zu erwarten.

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LES CHAINES TROPHODYNAMIQUES MARINES EXPERIMENTALES: METHODE D'ETUDE DES EFFETS PATHOLOGIQUES CONSECUTIFS AUX POLLUTIONS CHIMIQUES

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RESUME

Le milieu marin est susceptible de concentrer par l'intermédiaire des différents échelons de la biomasse, les produits chimiques qui y sont rejetés, pouvant aboutir ainsi à des phénomènes toxiques chez le consommateur de ces espèces.

Pour étudier ces processus, nous avons mis au point une méthode originale qui, en laboratoire, utilise diverses chaînes trophodynamiques.

Cette méthodologie, employée systématiquement, permet de mesurer les destructions de la biomasse, mais également d'apprécier les dangers vis-à-vis de la Santé Publique que peuvent créer des phénomènes de concentration de substances toxiques.

ABSTRACT

Marine organisms of various levels of the biomass are able to concentrate chemicals which are disposed of into the sea, and this can give rise to toxic effects in the consumer of these species.

To study these processes we have developed an original

laboratory method which makes use of various food chains.

Used systematically, this method permits measurement of the destruction of biomass, and makes it possible to assess hazards to public health which may arise from the concentration of toxic substances.

Le danger des pollutions chimiques de la mer tient aux capacités de concentration de certains de ces polluants au niveau d'espèces marines. Ce fait peut entraîner des taux élevés de ces substances souvent toxiques, principalement dans les derniers échelons des chaînes biologiques, qui sont habituellement livrés à la consommation.

Il y a plusieurs années, nous avons mis au point une méthode originale qui consiste à recréer en laboratoire des chaînes trophodynamiques marines, typiques des principales biocénoses, à leur soumettre pendant des temps plus ou moins prolongés et à des concentrations progressives les produits polluants que l'on désire étudier et à en lire les résultats à travers le comportement biologique et l'imprégnation chimique de leurs constituants.

Cette méthodologie, que nous utilisons d'une manière systématique, permet :

- de mesurer la destruction produite au niveau d'organismes-types représentant divers échelons les plus caractéristiques de chaînes trophodynamiques marines. Par ce moyen, il est possible d'évaluer la destruction en capital des ressources biologiques de la mer ;
- de tenir compte de l'ensemble des phénomènes de concentration et de biodégradation des substances chimiques soumises à ces tests et de juger des effets biologiques induits par la toxicité initiale ou secondairement apparus, ces produits chimiques passant à travers le milieu et étant absorbés successivement par les divers éléments vivants ;
- enfin, par l'introduction d'un consommateur final mammifère, de juger des phénomènes toxiques en fin de chaîne et de mesurer le danger encouru par l'Homme nourri de produits marins pollués. Cet aspect hygiéniste débouche ainsi sur les impacts de la pollution marine vis-à-vis de la Santé Publique.

C'est ainsi que nous avons mis au point quatre types de chaînes trophodynamiques :

- la chaîne de type pélagique, c'est-à-dire :
  phytoplancton - zooplancton - poissons - mammifères ;
- la chaîne de type néritique à mollusques, c'est-à-dire :
  phytoplancton - mollusques - mammifères ;
- la chaîne de type néritique à crustacés, c'est-à-dire :
  micro-organismes marins - invertébrés - crustacés - mammifères ;
- la chaîne de type benthique, comprenant :
  micro-organismes marins - invertébrés - poissons benthiques - mammifères.

Ainsi, une chaîne biologique peut être utilisée à différentes fins :

1) *Recherche des seuils de toxicité*

En mettant en contact chacun des échelons de la chaîne envisagée avec le polluant (produit chimique pur ou effluent industriel) à différentes concentrations, on peut déterminer avec une assez grande précision la sensibilité de chaque espèce à ce polluant. On peut ainsi définir pour chaque échelon un seuil toxique.

Les résultats permettent donc une prévision à court terme des conséquences du rejet de ces polluants en mer sur la survie des espèces et de définir les risques de perte en capital nutritionnel.

2) *Recherche des effets de la biodégradation d'un polluant*

Lors de son rejet en mer, un polluant peut servir de substrat aux bactéries marines et donc subir une biodégradation. Un tel effet peut entraîner une variation de la toxicité du polluant vis-à-vis des différents échelons marins de la chaîne biologique.

Les résultats rendent compte de la variation de la toxicité d'un polluant après contact avec l'eau de mer.

3) *Recherche du transfert et de la concentration de substances toxiques*

Ayant déterminé les seuils de toxicité directe d'un effluent, nous choisissons la concentration maxima permettant la survie totale de tous les échelons de la chaîne marine : de cette façon, la substance toxique pourra être transmise d'un échelon à l'autre, et éventuellement concentrée au cours des différentes étapes sans que la chaîne biologique soit rompue par la mort d'un des intermédiaires.

Les résultats permettent d'évaluer les risques de la consommation par l'Homme des produits marins et ainsi les dangers éventuels vis-à-vis de la Santé Publique.

VERSUCHE ZUR MEDIZINISCHEN BEDEUTUNG DES GLEICHFELD- ODER FARADAY-EFFEKTES; BAUTECHNISCHE FOLGERUNGEN

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KURZFASSUNG

Mäuse wurden unter der Einwirkung verschiedener bioklimatologischer Umweltbedingungen (elektrostatische Gleichfelder mit Feldstärken von: 40, 200, 1000, 5000, 24 000 V, normales Raumklima eines Labors, Faraday-Käfig) mit Hammelerythrozyten vorbehandelt, und es wurde der Immunisierungsgrad mit Hilfe der direkten Plaque-Technik nach JERNE ermittelt. Die höchsten Plaquebildungszahlen zeigten sich bei Milzen der im Gleichfeld lebenden Tiere, die niedrigsten Werte wurden dagegen unter feldlosen Umweltbedignungen gefunden. Dieselben Resultate in Form von Höchstwerten im Gleichfeld und Tiefstwerten im Faraday-Raum lieferten auch die Bestimmungen der jeweiligen Milzgewichte, Milzzellzahlen und Hämagglutinationstiter. Mögliche praktische Folgerungen werden diskutiert.

ABSTRACT

Mice previously treated with sheep erythrocytes were subjected to various bioclimatic conditions (constant electrostatic fields of 40, 200, 1000, 5000 and 24 000 V; normal laboratory environmental conditions; Faraday cage), and the levels of immunisation was determined by use of Jerne's direct plaque technique. The highest plaque formation counts were seen in the

spleens of animals living exposed to constant fields, and the lowest in animals in a field-free environment. Spleen weights, spleen cell counts, and haemagglutination titres showed a similar picture, with highest values under constant field and lowest values in the Faraday chamber. Possible practical conclusions are discussed.

Da die vielfältigen Möglichkeiten der technischen Zivilisation heute so tief in unseren Alltag eingreifen, können uns klimatologische Faktoren gerade dadurch stark beeinflussen. Bei unseren Versuchen kam es uns primär darauf an, mit exakt reproduzierbaren Versuchsbedingungen ebenso exakt faßbare Meßparameter zu erarbeiten, die, zumindest für einen klimatologischen Einzelfaktor, sichere Aussagen gestatten. In diesem Sinne befaßten wir uns mit der Luftelektrizität und hier speziell mit dem elektrostatischen Gleichfeld der Luft. (Gemeinsam m.Doz.Dr.Fischer).

Für diese Versuche an Kleintieren wurden in Zusammenarbeit mit Experten der Technischen Hochschule in Graz spezielle Versuchsanlagen angefertigt. (Gleichfeldkammern, Faraday-Kammern, Kontrollkammern).

Die Untersuchungen bewiesen vorerst, daß sich unter der Einwirkung verschiedener hochgespannter elektrostatischer Gleichfelder bzw. im Faraday-Raum die Meßparameter Motilität, Nahrungsaufnahme und Körpertemperatur, Sauerstoffverbrauch von Lebergewebe, sowie Glutamat- und Succinatdehydrogenase in Lebermitochondrien in signifikanter Weise änderten. Im Gleichfeld erfolgte dies in Form einer physiologisch als durchaus günstig zu interpretierenden Weise.

Die Abschirmung von elektrischen Feldern im Faraday-Raum bewirkte dagegen stets eine unvorteilhafte Reduzierung der genannten Stoffwechselmeßgrößen.

Recht vage Literaturberichte über günstige Allgemeineffekte elektrostatischer Gleichfelder auf Infektionen beim Menschen veranlaßten uns zu einer experimentellen Überprüfung dieser subjektiv qualitativen Beobachtungen, Gruppen von Mäusen wurden dazu mit Hammelerythrozyten immunisiert.

Den erzielten Immunisierungsgrad bestimmten wir mit Hilfe der direkten Plaque-Technik nach Jerne (Abb.1).

Die höchsten Plaquewerte und somit der stärkste Immunisierungsgrad ergaben sich zwischen 1000 und 5000 V/m, d.h. nur unter Einwirkung eines ganz bestimmten Feldstärkebereiches. Selbst die, natürlichen Durchschnittswerten bei ungestörten atmosphärischen Bedingungen entsprechende

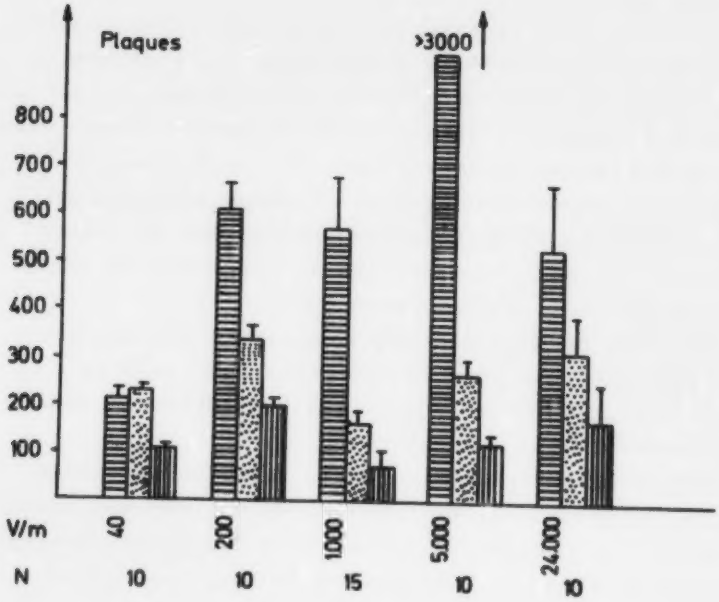

Abb. 1

Jerne-Test (direkt)

1. Kolumne (≡) = Gleichfeldkammer
   darunter Spannung in V/m
2. " (⁙) = Kontrollkammer
   (normale Laborgegebenheiten)
3. " (|||) = Faraday-Kammer

Feldstärke von 200 V/m führte noch, im Vergleich mit den Kontrollen, zu einem signifikanten Anstieg der Immunisierung. Unter den Werten natürlicher Gleichfelder liegende, niedrige Feldstärken führten zu keiner Erhöhung des Immunisierungsgrades. Die Abschirmung des Gleichfeldes in der Faraday-Kammer bewirkte stets weit unter der Norm liegende Plaquewerte.

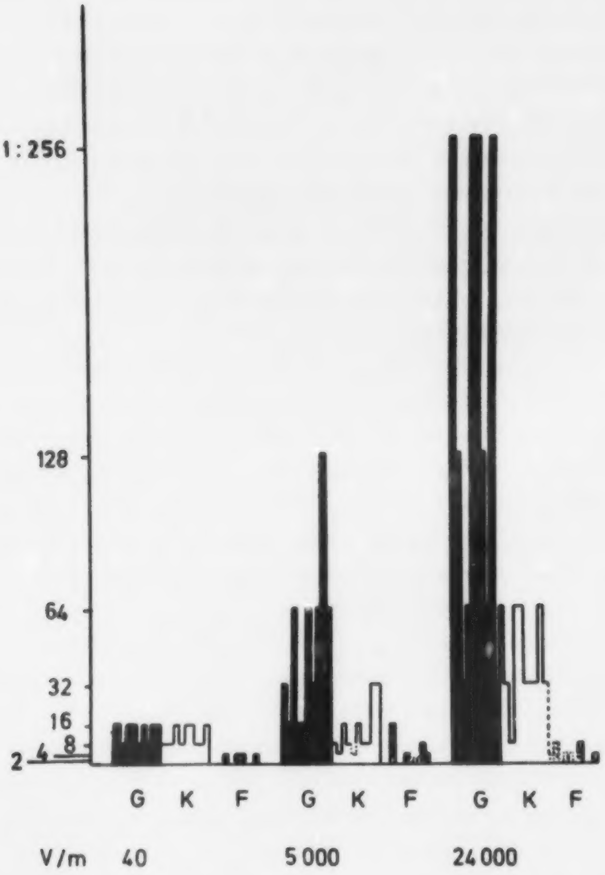

ABB. 2

Hämagglutinationstiter - je 10 Tiere pro Einzelversuchsgruppe

G = Gleichfeldkammer
darunter Spannung in V/m
K = Kontrollkammer (normale Laborgegeb.)
F = Faraday-Kammer

Gleichzeitig mit jedem Plaquetest durchgeführte Bestimmungen der entsprechenden Milzgewichte, Milzzellzahlen und Hämagglutinationstiter zeigten einen deutlichen Trend zur Übereinstimmung in Form einer generellen Zunahme im Gleichfeld und Abnahme unter feldlosen Umweltbedingungen. Diese Untersuchungen überprüfen und bestätigen die im Plaquetest erzielten Resultate (Abb.2).

Die Ergebnisse weisen darauf hin, daß das natürliche elektrostatische Gleichfeld der Erdatmosphäre einen bemerkenswerten Faktor zur Förderung der Bildung von Immunstoffen darstellt.

Wir wollen heute noch keine Schlußfolgerungen ziehen; aber alles weist darauf hin, daß man in Zukunft auch bei bautechnischen Überlegungen diese Verhältnisse weit mehr als bisher mitberücksichtigen sollte. Wir verbringen heute einen Großteil unseres Lebens in geschlossenen Räumen und es ist, wie unsere Versuche zeigen, durchaus nicht gleichgültig wie dabei klimatologische Faktoren geändert oder abgeschirmt werden.

Selbstverständlich haben diese Überlegungen vordringlich dort Gewicht, wo es um eine optimale Beeinflussung von Kranken geht, die erfahrungsgemäß auf negative bioklimatologische Einflüsse besonders ungünstig reagieren - z.B. in Intensivpflegestationen, Herzstationen, bei der prä- und postoperativen Behandlung etc.

Ich bin mir völlig bewußt, daß wir mit unseren Versuchen nur einen Teil bioklimatologischer Einflüsse erfaßt haben; die Ergebnisse sind aber derartig eindeutig,daß man in Zukunft die Gesamtforschung auf diesem wichtigen Gebiet unbedingt wird intensivieren müssen.

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METHODOLOGY OF EXPERIMENTAL AND EPIDEMIOLOGICAL RESEARCH OF DIFFERENT ENVIRONMENTAL PHYSIOPATHOLOGICAL FACTORS

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ABSTRACT

The multiplicity of the environmental factors and the diversity of their points of impact on the existential and evolutive states of living beings must not lead to neglect of physical, chemical, biological and statistical principles, the synthetical application of which constitutes the basis of a methodology. A pluridisciplinary approach is necessary but its difficulty and its complexity should not be minimized.

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Introduction

The multiplicity of the environmental factors and the diversity of their sites of impact on the existential and evolutive states of living beings must not result in the neglect of physical, chemical, biological and statistical principles, the application of which constitutes the basis of a methodology. A pluridisciplenary approach is necessary but its difficulty and its complexity should not be minimized.

Historical

The possible interactions between man and his environment have always been a subject of interest. Reclus (1) and Dubos (2) quote Hippocrate's "Airs, waters and places" and Montesquieu's "de l'Esprit des lois"; Brunhes, Vidal de la Blache and Leroi-Gourhan in France have described the relationships between human ethnology and geography. According to Bernard and Ruffie (3) the stratification of human raciation results from geographic separation and from socioeconomic isolation [Israelites of the Kurdistan, Laurie (4)]. In a more restricted but more immediate domain, aviation, submarine and space experiments in which man is enclosed in a limited space have lead to the study of the effects of imposed thermal, physical and chemical constraints. In addition to classical meteorological factors (temperature, humidity, atmospheric pressure, static electricity and electromagnetic waves Tromp (5) and Rivolier (6)) technical progress, since the beginning of the Victorian era increased industrial pollution. But awareness of these dangers has only become real since the threat of the atomic bomb. Radioactivity measurements in different parts of the world have discovered unsuspected methods of propagation through aerial, water and biological media.

Research Objectives

Every substance or factor which is a possible risk to man's health or comfort or which can indirectly touch his natural, cultural or economic patrimony is considered an environmental nuisance. This definition, obviously of a general nature must be practically limited to the search for the pathological effects of contamination of water, air and food by chmeical, physical and biological agents.

Most of environmental nuisances are interdependent, for example alcohol, tobacco and traffic casualties.

The multiplicity of environmental factors has as a counterpart the variety of their physiopathological effects. Choices must be made. Short-term objectives (acute toxicity, morbidity and mortality, urban factor) have mostly an applied aspect. Long-term objectives (penetration, metabolism, target organs, enzymatic inhibition or induction, genetic and teratological consequences, mutations, interactions between physical and chemical agents) are more theoretical and require a fundamental farsighted approach.

Technical Procedures

Two distinct complementary methodologies are employed, one centred on man, the other on animal experimentation.

A-Human studies

They include geopathology, epidemiological surveys, analyses of pollution, accidents, and occupational risks.

Geopathology investigates the action of soils (rural, urban or industrial) on pathology (malaria, Burkitt's tumor, air pollution of the Maurienne valley) and on human ecology.

Prospective inquiries require a very large number of subjects if the pathological consequence is rare, sometimes more than 200,000 subjects. In retrospective inquiries the definition of a control group is difficult. For each sick subject of the survey a control of the same age, sex, socioeconomical, geographical and racial origin must be matched (7).

Epidemiological surveys can be divided into surveys of mortality and morbidity. In France a certain uncertainty persists in the diagnosis of lethality. Morbidity criteria are difficult: absenteeism, exposure to medical and pharmaceutic agents. The Swedish studies on homozygote and heterozygote twins have enabled examinations of genetic factors in environmental toxicology (smokers and non-smokers).

Occupational medicine necessitates a good knowledge of well specified environmental factors and investigates immediate preventive measures. They must be developed rapidly especially in view of the increase in the number of new synthetic chemicals and their potential pathology (skin or respiratory allergies: farmers, lungs, byssinosis, bird breeders disease).

Certain acute episodes or accidents (air pollution in London in 1952, Mimamata's disease, diethylstilboestrol genital cancers in young girls) are privileged observations.

B-Animal experimentation

Considered as the quickest and safest way to obtain data on acute or chronic toxicity, animal experimentation gives rise to specific difficulties. A 1/10,000 risk will necessitate treating 10,000 or 30,000 rats or mice, supposing that the effect is the same in these animals and in men. In fact teratogenic effects must be assayed on 4 or more different species of mammals (thalidomide). The choice of an "animal model" imposes certain constraints (guinea pigs for allergical studies). Rats and mice are genetically well determined, and can be obtained pathogen free, but repeated blood of tissue sampling requires larger animals. Allometrical laws (8,9) should be taken into account but only between certain limits (diameters of dust particles penetrating into the airways of different species. On small laboratory rodents, which have a short life-span, it is possible to study long-term effects of pesticides, food additives and ionizing radiations on longevity, fecondity, offsprings and population dynamics (10). They enable investigations of genetic factors to be made which more and more are shown to have a role in the multiple-factor etiology of many diseases (cancer, anti-alpha-1-trypsine and emphysema, (11). Within the same species it has often been demonstrated that in addition to strain, sex and age interfere in toxicity studies (12,13,14).

C-Statistical procedures

Statisticians must consider the possibility of interference of temporal trends (ultradian, circadian and infradian rhythms) (15)

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UTILISATION DE CULTURES DE TISSUS HUMAINS POUR LA RECHERCHE D'UNE EVENTUELLE SYNERGIE ENTRE LES EFFETS TOXIQUES DE DEUX SOLVANTS USUELS: LE TOLUENE ET LE BENZENE

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RESUME

L'adaptation de plans d'expérience factoriels aux cultures de cellules, d'origine humaine, permet l'étude des interactions complexes entre toxiques. La réalisation du plan se fait en soumettant des cultures, de façon répétée, à des combinaisons de doses des toxiques étudiés.

L'exploitation des données utilise la méthode des moindres carrés, en se fixant un certain nombre de conditions évidentes. L'action des toxiques et leur interaction sont soumises globalement au test F de Snedecor, avant de les comparer à la valeur zéro, pour chaque point de mesure, par le test t de Student.

Ce plan, appliqué aux mélanges benzène/toluène, à faible teneur de benzène, révèle, dans les intervalles de doses soumises à l'expérience, et pour les premières 24 heures:

- *une action benzène indépendante de la dose,*
- *une action toluène dépendante de la dose,*
- *une interaction complexe benzène/toluène qui, pour certaines doses caractéristiques, n'est pas significative. Lorsqu'il en est autrement, l'interaction se manifeste dans le sens d'une diminution de l'effet toxique.*

ABSTRACT

The adaptation of the factorial planning of experiments to human cell cultures makes it possible to study complex interactions between toxic substances. The cultures are exposed repeatedly to combinations of doses of the toxic substances under investigation.

The data are evaluated by the method of least squares, with a certain number of obvious conditions. The effects of the substances, and their interaction, are all submitted to the Snedecor F test before they are compared at the zero value, for each reading by Student's t test.

This plan, applied to benzene/toluene mixtures having a low benzene content, showed, for the doses tested and for the first 24 hours:

- *an effect of benzene independent of the dose,*
- *a dose-dependent effect of toluene,*
- *a complex interaction between benzene and toluene, which at certain characteristic doses was not significant. Otherwise, the interaction shows itself by a reduction of the toxic effect.*

1. Introduction

La recherche d'interactions complexes entre les effets toxiques de deux substances chimiques nécessite le traitement statistique d'un grand nombre de valeurs obtenues en combinant, deux à deux, un certain nombre de doses de substances étudiées, chaque cas devant être répété plusieurs fois. L'emploi des cultures de cellules rend cette recherche moins lourde que lorsqu'on utilise des animaux de laboratoire, technologiquement et financièrement. Elle peut se suffire à elle-même, si on ne s'intéresse qu'à la cytotoxicité, ou si le comportement des cultures, pour les toxiques considérés, est un bon modèle de ce qui a été observé en toxicité aiguë sur animal (D.Gradiski, J.L Magadur |1|). Dans les autres cas, elle peut servir de modèle à une expérimentation animale ultérieure ou être complétée par une simulation. L'état actuel de la technique, telle qu'elle est utilisée dans notre laboratoire, est exposé à propos de la recherche d'une éventuelle interaction benzène/toluène, dans les mélanges dans ces deux corps, à faible proportion de benzène.

2. Plan expérimental

Les deux toxiques sont considérés comme deux traitements (T = toluène ; B = benzène) dont les différentes doses représentent les degrés (K_T doses pour le toluène, K_B doses pour le benzène). Chaque combinaison de doses est répétée n fois.

Le paramètre observé est le nombre de cellules par ml, compté à la cellule "Nageotte". Chacune des mesures est repérée : $x_{i.j.r}$ $\left\{\begin{array}{l} 0 \leqslant i < K \\ 0 \leqslant j < K \\ 1 \leqslant r < n \end{array}\right\}$

Le modèle adopté est le suivant :

$$x_{ijr} = \mu + a_i + b_j + c_{ij} + \varepsilon_{i.j.r} \qquad (1)$$

où : μ est la moyenne des témoins non traités ($\overline{x}_{00}$),

a_i est l'écart par rapport à μ, dû à l'action du toluène,

b_j est l'écart par rapport à μ, dû à l'action du benzène,

c_{ij} est l'écart par rapport à μ, dû à l'interaction benzène/toluène,

ε_{ijr} est une réalisation de la variable gaussienne ε de moyenne nulle et de variance inconnue.

Le problème à résoudre s'énonce ainsi :

L'échantillon de mesure x_{ijr} dont on dispose, permet-il de réfuter l'existence des termes a_i, b_j et c_{ij}, avec une probabilité de se tromper inférieure au seuil α.

Le mode de résolution utilise la méthode des moindres carrés, en posant les relations évidentes $a_0 = 0$; $b_0 = 0$; $c_{i0} = 0$; $c_{0j} = 0$.

3. Manipulation

Les mises en cultures et traitements par les toxiques sont effectués comme décrit dans un travail précédent (D.Gradiski, J.L Magadur |1|). Les cellules appartiennent à la lignée Hela. Toutes les précautions sont prises pour ne pas introduire un facteur de variation non contrôlé. Les doses employées sont respectivement les suivantes (en moles/ml) :

Toluène : 0; $2,3.10^{-9}$; $2,3.10^{-8}$; $2,3.10^{-7}$

Benzène : 0; $2,7.10^{-11}$; $2,7.10^{-10}$; $2,7.10^{-9}$; $2,7.10^{-8}$; $2,7.10^{-7}$; $2,7.10^{-6}$

Chaque combinaison de doses est répétée trois fois. Les comptages sont effectués après 24, 48 et 72 heures. Seuls les résultats obtenus à 24 h sont discutés.

4. Résultats expérimentaux et traitement statistique

Il est impossible de fournir ici tous les résultats expérimentaux, de même que toutes les valeurs statistiques intermédiaires. Un double tableau présente (Fig. 1) : - dans la partie supérieure, de façon intuitive

. les résultats expérimentaux, exprimés en % d'inhibition de développement, par rapport aux cultures témoins (traits pleins),

. la surface théorique correspondant à un modèle purement additif (pas d'interaction) (tirets) ;

- dans la partie inférieure :

. les valeurs trouvées pour les différents a_i et b_j, termes d'action du benzène et du toluène (première colonne et première ligne),

. les valeurs trouvées pour les c_{ij} , termes d'interaction

5. Discussion

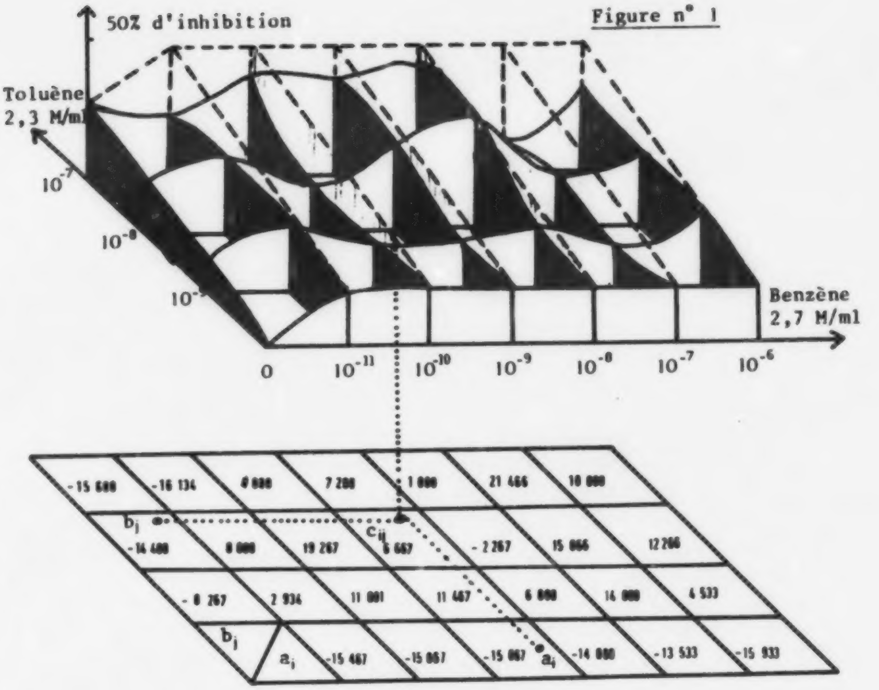
Le test F de Snedecor, effectué pour l'ensemble des résultats au premier jour, associé au test t de Student, pour rejeter l'hypothèse de nullité des a_i , b_j , c_{ij}, permet d'affirmer :

. que le benzène exerce une action sur le développement des cellules Hela ($p>0,95$). Dans l'intervalle de doses choisi, cette action atteint son maximum dès la première dose ;

. que le toluène exerce aussi une action ($p>0,95$) tendant vers une limite supérieure,

. qu'il existe une interaction benzène/toluène ($p>0,999$). Cette interaction n'est pas significative pour certaines combinaisons de doses (en particulier celles contenant 10^{-8} M/ml de benzène). Lorsqu'elle est significative elle s'exerce toujours dans le sens d'une diminution de l'effet toxique total.

Figure n° 1



-15 600	-16 134	8 000	7 200	1 000	21 466	10 000
-14 400	8 000	19 267	6 667	- 2 267	15 066	12 266
- 8 267	2 934	11 001	11 467	6 000	16 000	4 533
b_j / a_i	-15 467	-15 067	-15 067	-14 000	-13 533	-15 933

Légende : La projection d'un point de mesure sur la case correspondante du tableau inférieur permet de lire : dans cette case, le terme c_{ij} ; dans la colonne la plus à gauche, le terme b_j et dans la ligne inférieure, le terme a_i.

Quelques hypothèses peuvent être formulées, tendant à rendre compte de ces interactions. La recherche d'éléments expérimentaux nouveaux permettra de choisir la plus probable à la suite d'une simulation qui devra reproduire les faits expérimentaux exposés ici.

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EXPOSURE OF LABORATORY ANIMALS TO URBAN AIR POLLUTION: PHYSICAL PLANT, EXPERIMENTAL DIFFICULTIES, OBSERVED EFFECTS

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ABSTRACT

Approximately 3500 animals were involved in a 5-year experiment to determine the health effects of air pollution as it occurs in the center of a large city (Detroit). One-half of the animals breathed air from out-of-doors constantly, with the air delivered to them into chambers with as little change as possible except temperature control. The other half of the animals breathed air after passage through activated charcoal and fine pore filter banks. Elimination of various pollutants ranged from excellent (particulate matter, oxidants) through fair (nitrogen oxides, SO_2) to poor (hydrocarbons, CO). Several strains of mice, rats, rabbits and guinea pigs were exposed and studied during their lifetimes, in some cases including breeding and observation of progeny.

Mortality, morbidity, body weight, body temperature, electrocardiography, pulmonary function, the results of periodic blood tests including hemoglobin, hematocrit, and red blood cell count, and starch gel zymograms of esterase, lactate dehydrogenase, and acid phosphatase of pulmonary and lymphnode tissues showed no significant differences between the colonies. Histopathologic studies on various tissues were also unremarkable except for the

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amount of particulate matter present in the lungs. Possible effects of borderline significance included elevated plasma alkaline phosphatase in exposed rabbits and increased spontaneous activity (by running wheel) in young exposed mice. The only pronounced and sustained difference between the colonies was in the white blood cell count, attributable chiefly to an increase in the number of lymphocytes in the exposed animals.

The health effects of urban air pollution were studied intensively in recent years by means of human epidemiology[1] and animal experiment [2]. During the years 1960-65, a study involving the latter approach was conducted at Wayne State University in Detroit, under auspices of the U. S. Public Health Service[3].

The guiding principle of the Detroit study was to expose a colony of experimental animals to ambient levels of air pollution as it occurs at a busy downtown intersection with as little change as possible and compare the long-range health status of these animals to that of an identically maintained control colony which breathed as clean air as it was possible to obtain. An extensive physical plant was constructed in order to realize these objectives (Figs. 1, 2). Street air was sucked into a 60 cm diam.

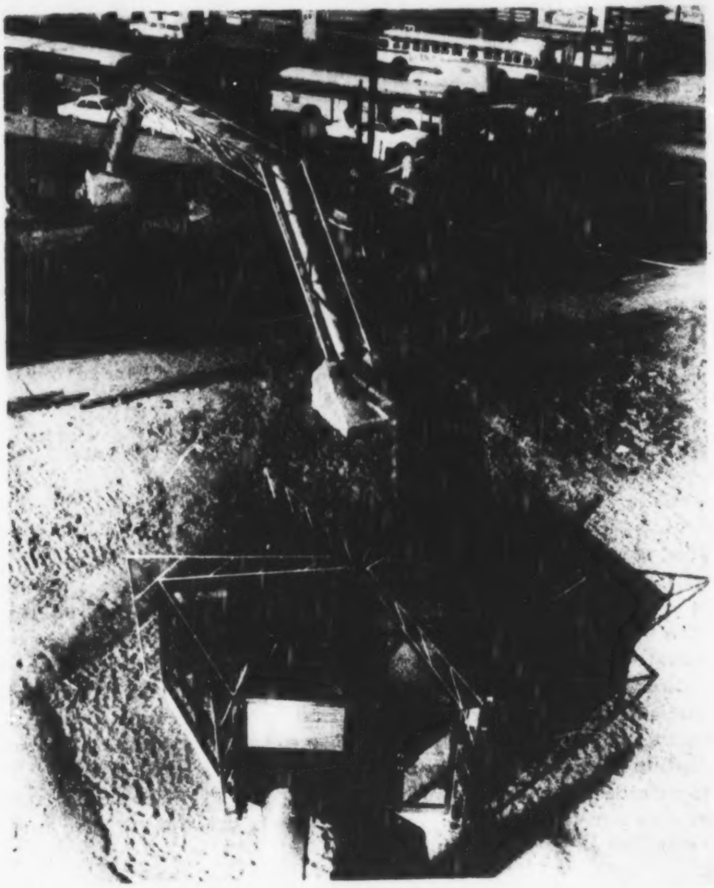

Fig. 1. Air pollution intake duct and fan house, top view.

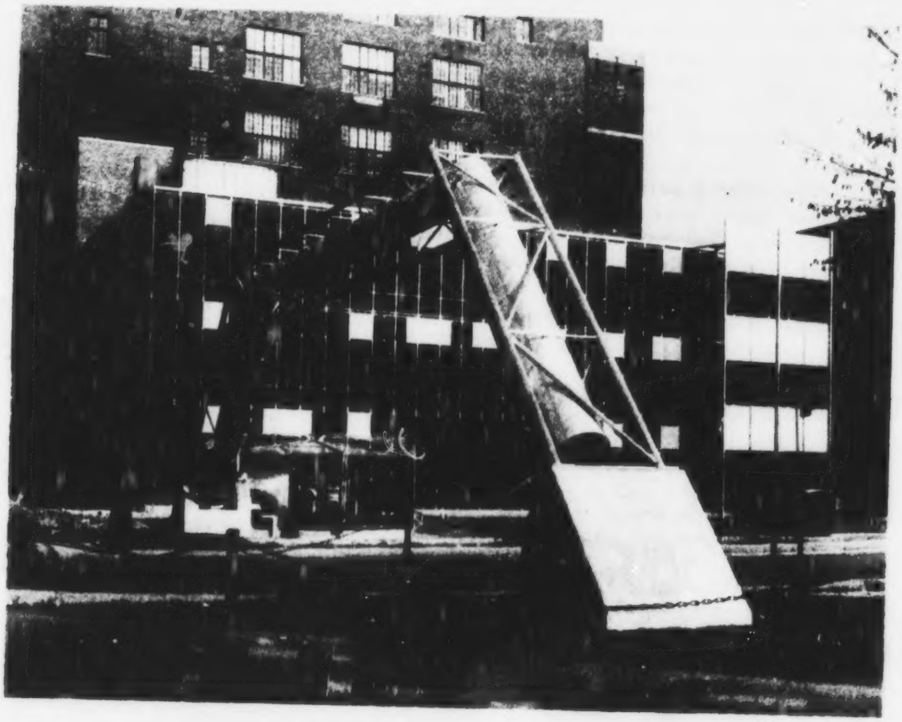

Fig. 2. Air pollution intake duct, fan house, and laboratory building, horizontal view.

duct which arched over a street at a height of 4.4 m with 22 inlet holes. The air passed through a fan house where it was heated or cooled according to the season and then delivered into the laboratory building where the animal rooms were located. For the ambient air room the tempered air was delivered directly through a perforated wall. For the clean air room, the airstream was passed through a set of absolute filters and activated charcoal absorbers and subsequently delivered through another perforated wall. The air was exhausted from each animal room through the opposite perforated wall, with a second fan located in the discharge duct. A pressure balance was maintained at a slightly positive level in order to minimize outside contamination of the animal rooms through the doors. The system was capable of handling 100-350 m^3 air per minute, depending on the outside temperature, resulting in 60-180 air changes per hour. Delivery of outside air into the animal rooms took no more than 5 seconds so that changing outside conditions due to varying traffic patterns were faithfully reflected in the experiment.

Table 1 illustrates the degree of success of the physical plant. First, it can be seen that ambient air room levels resembled outside

Table 1
Instrumental Analysis of Air Quality

Contaminant	Unit	Typical Monthly Means		
		outside building	ambient air room	clean air room
Total particulate	γ/m^3	95	91	1.4
Total oxidant	p.p.h.m.	0.5	0.6	0.05
Total hydrocarbon	p.p.m.	2.6	2.7	2.5
CO	p.p.m.	3.2	3.1	3.0
SO_2	p.p.h.m.	10	8.8	5.1
NO_2	p.p.h.m.	5.7	6.5	1.7
NO	p.p.h.m.	9.0	11.2	14.2

levels for all contaminants, so that the atmosphere was indeed delivered to the animals with no substantial change. Second, it can be seen that with respect to difference between the ambient air and clean air rooms, the contaminants may be divided into 3 groups. Substantial concentration differential was seen with particulate matter and oxidant only. Moderate concentration differential was seen with SO_2 and NO_2. Essentially no concentration differential was seen with CO and hydrocarbons. An anomalous situation existed with respect to NO, which was apparently created during the cleansing procedure, resulting in higher concentration in the clean air room than in the ambient air room. The two nitrogen oxides together underwent moderate reduction of concentration during filtering.

The experimental animals exposed to these atmospheres included 650 mice, 600 rats, 400 guinea pigs, and 100 rabbits of various strains in each colony. The animals were kept in their respective exposure rooms throughout their lifetimes, in some cases including breeding and observation of progeny. Air pollution created by their own excrements was carefully controlled by a thorough sanitation schedule. Feeding, watering, sample collection, and other handling was strictly identical for the two colonies.

It was recognized that filtering of air involved removal of microbiological contamination as well, and since this was not one of the desired variables the incidence of infectious conditions had to be equalized in the two colonies. For this purpose, 25-50 additional animals of each species were designated as "bacterial flora carriers" and alternated between the exposure rooms on a daily basis. The latter animals were otherwise not evaluated in the experiment. Equalization of bacterial flora was satisfactory as evidenced by very nearly identical mortality and gross morbidity rates between the colonies for each species.

In order to monitor subtle manifestations of morbidity or other physiological responses attributable to air pollution, an animal testing schedule was established involving physiological measurements on a multichannel analyzer and blood tests including hematocrit, hemoglobin, cell counts, and serum electrophoresis. At periodic sacrifices, lung and tracheobronchial lymph node tissues were obtained and examined histopathologically and biochemically. Mice had voluntary exercise wheels in their cages with automatic revolution counting devices.

The summary results on all these measurements (Table 2) showed that the only really significant difference between the animal colonies was in the particulate load of the lungs (attributable chiefly to increased levels of aluminum, barium, and lead in the exposed animals); and in the white blood cell counts (attributable chiefly to increased number of lymphocytes in the exposed animals). Small increases of questionable significance were also seen in the serum alkaline phosphatase levels of rabbits and in the voluntary activity of young mice. Unaffected were essentially all other measured parameters including specifically the physiologic and histopathologic evaluations of animal health.

Table 2

Measurable Differences Between Animal Colonies*

Parameter	Typical Monthly Means	
	ambient air	clean air
Rat WBC counts, x10^3(with lymphocyte %)	8. 6(78)	7. 6(73)
Guinea pig WBC counts, x10^3(with lymphocyte %)	8. 2(61)	7. 3(56)
Rabbit WBC counts, x10^3(with lymphocyte %)	4. 8(62)	3. 6(56)
Rabbit serum alk. phosphatase(KA units/100 ml)	5. 90-6. 21	5. 73-5. 77
Rabbit lung ash, Al (p. p. m.)	249	170
Rabbit lung ash, Ba (p. p. m.)	5. 6	2. 9
Rabbit lung ash, Pb (p. p. m.)	23. 5	10. 4
Mouse voluntary activity (10^3 revs. /wk.)	29	27

*Lack of reproducible differences was experienced with respect to the following parameters: Body weight; body temperature; electrocardiogram; pulmonary function; kind and degree of pulmonary histopathology; plasma electrophoresis; isozymes of esterase, acid phosphatase and lactate dehydrogenase; hemoglobin; hematocrit; erythrocyte counts; and the following elements in lung tissue: Cr, Co, Cu, Mn, Mo, Ni, Sr, Sn, Ti, V, and Zn.

The increased particulate load of the lungs was a natural consequence of breathing unfiltered air and the increased lymphocyte counts probably reflected a phagocytic response to this challenge. This is a normal defense mechanism of the respiratory system and it appears that the physiologic reserves of the organism were not exhausted by the exposure. It may be concluded that breathing ambient city air did not measurably impair the health of these animals. However, the increased heavy metal burden in the lungs is remarkable and the possible chronic effects of this accumulation were not evaluated in this study.

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EFFETS SYNERGIQUES DES POLLUANTS PARTICULAIRES ET D'INFECTIONS EXPERIMENTALES TUBERCULEUSE OU ORNITHOSIQUE

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RESUME

Plusieurs types de modèles expérimentaux sont réalisés, comportant des empoussiérages de particules minérales diverses associés à des infections de natures différentes. Deux types de contaminations bactériennes sont réalisées, soit par voie intro-veineuse pour l'infection tuberculeuse (Mycobactérium Kansasii) soit par voie intra-péritonéale pour l'agent de l'ornithose.

Les résultats obtenus montrent une aggravation indiscutable des infections pulmonaires ou générales par les poussières. Toutefois cette aggravation est commandée par:

- *la nature de l'agent infectant et l'existence ou non d'une phase de parasitisme cellulaire obligatoire;*
- *la nature et la nocivité cellulaire propre de chaque poussière;*
- *la quantité totale de particules retenues au niveau du poumon dans le cas des infections de nature tuberculeuse.*

Les mécanismes primaires responsables des phénomènes d'aggravation n'apparaissent pas univoques. Ils sont ainsi liés au point d'impact particulier et au mode de multiplication spécifique de chaque agent infectant d'une part et à la cytotoxicité propre de chaque poussière d'autre part. Ils conditionnent ainsi le type de réaction et les effets synergiques constatés.

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Les nombreux travaux consacrés indépendamment à l'action des polluants minéraux et aux diverses infections pulmonaires ont permis de mieux connaître la nocivité et la pathologie particulaire liée à chacun de ces agents.

Néanmoins, il est fréquent sinon habituel en pathologie humaine, surtout dans certaines activités industrielles, de voir se combiner au niveau pulmonaire notamment, l'action d'agents pathogènes multiples. Ainsi en est-il des polluants particulaires minéraux et des infections. C'est à quelques-uns de ces effets synergiques que se rapporte ce travail.

ABSTRACT

Various types of experimental model were constructed for exposure to various mineral dusts associated with different types of infection. Infection was induced either by the intravenous injection of tuberculosis (Mycobacterium kansasii) or by the intraperitoneal injection of ornithosis.

The results showed a definite aggravation of pulmonary or general infections by the dusts. However, the aggravation depended on:

- *the nature of the infective agent, and the presence or absence of a phase of obligatory cellular parasitism;*
- *the nature of each dust and its ability to damage cells;*
- *the total quantity of particles retained in the lung in the case of tuberculous infections.*

The primary mechanisms responsible for the aggravation phenomena appear to be somewhat ambiguous. For example, they are linked on the one hand with the point of impact concerned and the specific mode of multiplication of each infective agent,

and on the other with the specific cytotoxicity of each dust. In this way they condition the type of reaction and the synergistic effects which are observed.

Numerous individual studies relating to the effects of mineral pollutants or to various pulmonary infections have provided further knowledge of the noxiousness and pathology specific to each of these agents.

Nevertheless, it is the combined effects of a number of pathogenic agents which are observed frequently if not regularly, notably in the human lung, in the context of certain industrial activities. The same is true of particulate mineral pollutants and infections. The present study is concerned with some of these synergistic effects.

1. Méthodes expérimentales

1.1 - Poussières

Les différentes poussières (charbon, quartz, oxyde de titane, chrysotile) utilisées sont des particules inférieures à 5 microns. Elles sont administrées soit par empoussiérage dans des cages CERCHAR à régulation automatique, soit en suspension dans un liquide physiologique dans le cas d'injections péritonéales.

1.2 - Infection

Deux types de germes ont été inoculés :

- soit par injection intra-veineuse pour Mycobactérium Kansasii ;
- soit par voie intra-péritonéale pour l'agent de l'ornithose (Chlamydia psittaci).

Les animaux ont été choisis en fonction de leurs sensibilités aux différents germes : cobayes pour l'infection mycobactérienne, souris IOPS-OF pour l'ornithose.

2. Résultats

2.1 - Empoussiérage et infection mycobactérienne (Mycobactérium Kansasii)

Les animaux ont été empoussiérés avec des mélanges charbon-quartz, à raison de 300 mg/m3 d'air, pendant des périodes de temps variables, de façon à obtenir des charges pulmonaires progressivement croissantes. Deux séries ont été réalisées, comportant des mélanges charbon-quartz à faible et forte teneur en quartz. Les résultats obtenus six semaines après l'inoculation bactérienne sont représentés dans le tableau I. Ils montrent :

- l'aggravation nette des lésions tuberculeuses par l'empoussiérage préalable, aggravation jugée sur le pourcentage de la surface des lésions histologiques pulmonaires et sur le nombre de mycobactéries viables réisolées des poumons après 6 semaines d'évolution ;
- l'augmentation proportionnelle des lésions en fonction de la quantité de poussières présentes dans les poumons ;
- à quantité égale, que la présence de particules à nocivité cellulaire élevée (quartz) dans un mélange de poussières aggrave de façon importante le développement des lésions tuberculeuses.

2.2 - Empoussiérage et infection ornithosique (Chlamydia psittaci)

La suspension infectante est obtenue à partir du sac vitellin d'oeufs embryonnés. Après centrifugation la suspension riche en corps élémentaires est inoculée par voie intra-péritonéale à la souris après titration de l'inoculum sur cellules L en couches monocellulaires.

TABLEAU I

Influence de la charge coniotique et de la teneur en quartz sur l'infection tuberculeuse

Poussières	% de quartz dans les poumons	Charge pulmonaire en poussières en mg	Dose de Mycobactérium Kansasii	Indice histo. des lésions	Nombre de bacilles réisolés	
Mélanges à faible teneur en quartz	3,2	13,4	8.10^5	1,4	50	x10^3
	5,1	26,6		7	30	
	5,7	34,5		13,2	424	
	5	62,2		12,8	462	
	6	83,5		24,9	676	
Mélanges à forte teneur en quartz	6,2	38,7	$6,5.10^5$	2,2	45	10^3
	11,5	23,8		0,9	86	
	12,8	33		5,2	1.295	
	15,7	44		4,2	1.425	
	64,5	34,3		14,5	3.765	

TABLEAU II

Pourcentage de souris survivantes après empoussiérage et infection par Chlamydia psittaci - (8 U.I.)

	Dose infectante	Pourcentage de survie	
		au 8è jour	au 10è jour
Ornithose	10^{-2}	80	70
Quartz + Orn.	10^{-2}	60	50
Charbon + Orn.	10^{-2}	30	20
Charbon témoin	--	100	100
Quartz témoin	--	100	100
Ornithose	10^{-1}	90	90
TiO_2 + Orn.	10^{-1}	85	74
Chrysotile + Orn.	10^{-1}	4	4
TiO_2 témoin	--	100	100
Chrysotile témoin	--	100	100

Les poussières minérales utilisées (quartz, charbon, oxyde de titane, chrysotile) sont broyées et triées en particules $< 5\ \mu$. Elles sont ensuite injectées par voie péritonéale à la dose de 20 mg par animal.

Les résultats exprimés en pourcentage de survie des animaux sont exprimés dans le tableau II. On remarque que la seule injection de particules minérales n'entraîne aucune mortalité. Par contre, pour les animaux inoculés avec l'agent de l'ornithose, l'injection préalable d'une poussière entraîne une aggravation de la maladie ornithosique qui se traduit par une accélération dans l'apparition des symptômes de la maladie et par une augmentation du taux de mortalité. On constate d'autre part que cette aggravation est variable suivant la nature de la poussière utilisée (tableau II). Elle est ici moins importante pour le quartz, minéral à toxicité cellulaire élevée, que pour le charbon. Ce phénomène est probablement en relation avec la phase de parasitisme cellulaire obligatoire de Chlamydia psittaci, celle ci ne pouvant se produire en raison de la lyse importante des macrophages péritonéaux provoqués par le quartz.

Ces résultats, obtenus au niveau pulmonaire ou péritonéal, sont représentatifs de l'action aggravante de la poussière sur certaines infections expérimentales. Ils demanderaient toutefois, avant d'être généralisés une étude plus étendue, notamment avec différents types d'infections, dont les modalités de développement peuvent s'avérer extrêmement variables d'un germe à l'autre.

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LES EFFETS DES POLLUANTS SUR L'EPURATION PULMONAIRE

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RESUME

L'épuration pulmonaire a été mesurée chez différentes espèces animales: chat, rat, singe, soit dans des conditions normales en vue d'en préciser les principaux mécanismes, soit sous l'action de divers polluants particulaires ou gazeux. Deux méthodes comportant une inhalation unique ou répétée de poussière ont été utilisées: l'une consiste à doser les poussières dans les poumons des animaux sacrifiés par lots en fonction du temps; l'autre nécessite l'emploi d'une poussière marquée (hématite marquée au ^{59}Fe), la radioactivité intra pulmonaire étant mesurée par des comptages externes.

Cette deuxième méthode a servi également à faire des mesures de rétention et de capacité d'épuration chez l'homme, les doses de poussière marquée étant très faibles (inférieures à 1 microcurie).

Les résultats obtenus permettent de faire les constatations suivantes:

- il existe des différences importantes dans la vitesse d'épuration selon la nature des poussières et selon l'espèce animale considérée. La différence est peu importante au niveau de l'épuration bronchique qui est très rapide; par contre au niveau alvéolaire, la vitesse d'épuration varie dans une large proportion: rapide chez le chat, elle est très lente chez l'homme.

On constate en outre une variation individuelle importante au sein d'une même espèce.

- la capacité d'épuration pulmonaire mesurée chez le rat est nettement affectée par des inhalations antérieures de poussières qui ont pour effet de ralentir le phénomène d'autant plus fortement que la charge coniotique est plus élevée.

- les gaz irritants tels que les vapeurs nitreuses et l'anhydride sulfureux tendent à favoriser légèrement l'élimination des poussières intra-alvéolaires.

ABSTRACT

Pulmonary clearance was measured in various animal species (cat, rat, monkey) either under normal conditions, to determine the principal mechanisms, or under the influence of various particulate or gaseous pollutants. Two methods were used, entailing a single inhalation or repeated inhalations. The first consists in determining the quantity of dust in the lungs of groups of animals sacrificed after various time intervals, and the second is based on the use of a labelled dust (^{59}Fe - labelled haematite) and the determination of intra-pulmonary radioactivity by external counting.

The second method was also used to measure retention and clearance capacity in man, using minute quantities of labelled dust (less than 1 microcurie).

The results obtained permitted the following conclusions:

- The rate of clearance varies considerably according to the type of dust and the animal species in question. Bronchial clearance is rapid, and the differences are slight; the rate of alveolar clearance on the other hand, varies considerably, being rapid in the cat and very slow in man. There are also considerable individual variations within a given animal species.

- Clearance capacity measured in the rat was clearly af-

fected by prior inhalation of dust; the slowing down of the clearance process becomes more marked as the quantity of dust increases.

- Irritant gases, such as nitrous oxide and sulphur dioxide, show a slight tendency to favour the elimination of dust from within the alveoli.

1. Introduction

Les recherches consacrées depuis plusieurs années à l'épuration pulmonaire ont permis d'en préciser les principaux mécanismes et d'en établir les lois, mettant notamment en évidence l'existence d'une épuration bronchique rapide et d'une épuration alvéolaire lente.

Cette dernière présentant une importance particulière en ce qui concerne la genèse des lésions pulmonaires d'origine coniotique, il a paru essentiel de tenter d'en déterminer les caractéristiques et les variations individuelles, ainsi que d'analyser les modifications qu'elle peut subir du fait de différentes agressions d'origine extérieure ou encore de certaines lésions de l'appareil pulmonaire lui-même.

2. Méthode expérimentale

Les recherches ont été menées sur trois espèces animales : le chat, le rat et le singe, ainsi que sur l'homme.

2.1 - Poussières

L'empoussiérage pulmonaire est réalisé par inhalation d'une suspension de particules inférieures à 5 µ à la concentration de 300 mg/m^3 dans des cages à régulation automatique. Quatre types de poussières ont été étudiés : le quartz, le charbon, l'oxyde de titane et l'hématite.

2.2 - Gaz

Deux gaz irritants ont été testés : les vapeurs nitreuses et l'anhydride sulfureux. L'inhalation de NO_2 a été réalisée par bouffées de 30 minutes (concentration de 100 à 30 ppm) pendant 3 heures par jour et l'inhalation de SO_2 à la concentration de 300 ppm à raison de 2 heures par jour.

2.3 - Contrôle de l'épuration pulmonaire

Les caractéristiques d'épuration vis-à-vis d'une poussière donnée ont été déterminées en suivant l'élimination de la poussière par des dosages chimiques dans les poumons après sacrifice de l'animal.

L'influence des gaz irritants sur la vitesse d'épuration des poussières inhalées a été mesurée selon le même procédé.

Enfin, l'étude cinétique de l'épuration pulmonaire normale et des modifications qu'elle subit sous l'action de divers facteurs : nature de la poussière, charge coniotique, a été faite par inhalation de poussières d'oxyde de fer Fe_2O_3 marqué au ^{59}Fe puis comptage de la radioactivité γ intrapulmonaire.

3. Caractéristiques de l'épuration

3.1 - Variation selon la nature des poussières

TABLEAU I

Influence de la nature
des poussières sur leur vitesse d'épuration

Nature de la poussière	Pourcentage épuré après 46 jours	
	chat	rat
quartz	45	25
charbon	84	< 5
oxyde de titane	70	23
hématite	76	55

TABLEAU II

Taux de rétention globale et vitesse d'épuration
alvéolaire chez l'homme. Variations individuelles.

Sujet	Rétention globale en % de l'aérosol mis en suspension	Taux de rétention alvéolaire (en % de la rétention totale)	Période de l'épuration alvéolaire (en jours)
L...	5,9	90	100
B...	8,5	68	117
S...	3,8	80	183
H...	4,4	76	280
M...	7,2	82	560

Les résultats de l'étude effectuée sur le chat et sur le rat avec des poussières de quartz, de charbon, d'oxyde de titane et d'hématite sont portés dans le tableau I. Il apparaît une nette influence de la nature chimique des poussières sur leur taux d'épuration. On observe en outre que le classement des poussières en ce qui concerne leur vitesse d'élimination n'est pas le même d'une espèce à l'autre. En particulier, l'épuration du charbon est rapide chez le chat tandis qu'elle est très faible chez le rat.

3.2 - Variation selon l'espèce

La différence de vitesse d'épuration d'une même poussière selon l'espèce animale considérée a été étudiée en utilisant de l'hématite marquée chez le chat, le rat et le singe et une comparaison a été faite avec l'homme. L'épuration des voies respiratoires supérieures et des bronches apparaît rapide dans tous les cas (période inférieure à 2 jours) tandis que l'épuration alvéolaire varie de façon importante d'une espèce à l'autre, comme le montrent les courbes de la figure 1. Les périodes moyennes correspondantes ont été calculées : 16 jours pour le chat, 28 jours pour le rat, 250 jours pour l'homme, 300 jours pour le singe.

3.3 - Variations individuelles

Une étude antérieure effectuée sur le chat au moyen d'hématite marquée avait montré l'existence de variations individuelles de la courbe d'épuration. On a déterminé par la même méthode les variations individuelles du taux de rétention et de la vitesse d'épuration chez l'homme. Les résultats portés dans le tableau II et concernant cinq sujets testés dans des conditions d'essai identiques montrent d'une part que la rétention globale varie dans des proportions importantes, d'autre part qu'il existe des différences de l'ordre de 1 à 5 dans les vitesses d'épuration alvéolaire.

4. Action des polluants sur la capacité d'épuration

4.1 - Polluants particulaires

L'étude, effectuée sur le rat, a porté sur trois sortes de poussières : le charbon, l'oxyde de titane et l'hématite. Après inhalation de quantités variables de poussières, la capacité d'épuration a été testée à l'hématite marquée. Le tableau III montre que l'inhalation de poussières, de quelque nature qu'elles soient, diminue la capacité d'épuration vis-à-vis de nouvelles particules atteignant le poumon. Cette diminution est d'autant plus marquée que la charge coniotique est plus élevée. On constate en outre que le retour à la capacité normale d'épuration dépend de la nature des poussières : dans le cas présent, il n'est observé que pour l'oxy-

TABLEAU III

Action des polluants particulaires sur la capacité d'épuration pulmonaire du rat

Nature du polluant	Charge coniotique par poumon après empoussiérage (mg)	Période de l'épuration alvéolaire (en jours) après différents délais d'évolution (1)				
		0	3 mois	6 mois	9 mois	18 mois
charbon	2,7	69	-	28	-	-
	8,1	72	-	49	-	-
	30,9	365	-	-	-	277
oxyde de titane	4,9	27	22	-	20	-
	11,2	55	47	-	28	-
	20	95	63	-	32	-
hématite	5,4	-	21	-	19	-
	25,6	-	136	-	87	-
	51,6	-	154	-	124	-

(1) période moyenne des témoins : 25 jours

TABLEAU IV

Influence de l'inhalation de gaz irritants chez le rat (NO_2, SO_2) sur l'épuration pulmonaire des poussières

Nature de la poussière	Nature du gaz et conditions d'inhalation	Taux d'épuration après 4 semaines		Variation du taux d'épuration
		Témoin	NO_2	
Charbon-quartz (témoin : 2,9 mg par poumon)	NO_2 après empoussiérage	8,6 %	22,4 %	+ 160 %
Oxyde de titane (témoin 4,4 mg par poumon	SO_2 après empoussiérage	46,6 %	50 %	+ 7 %

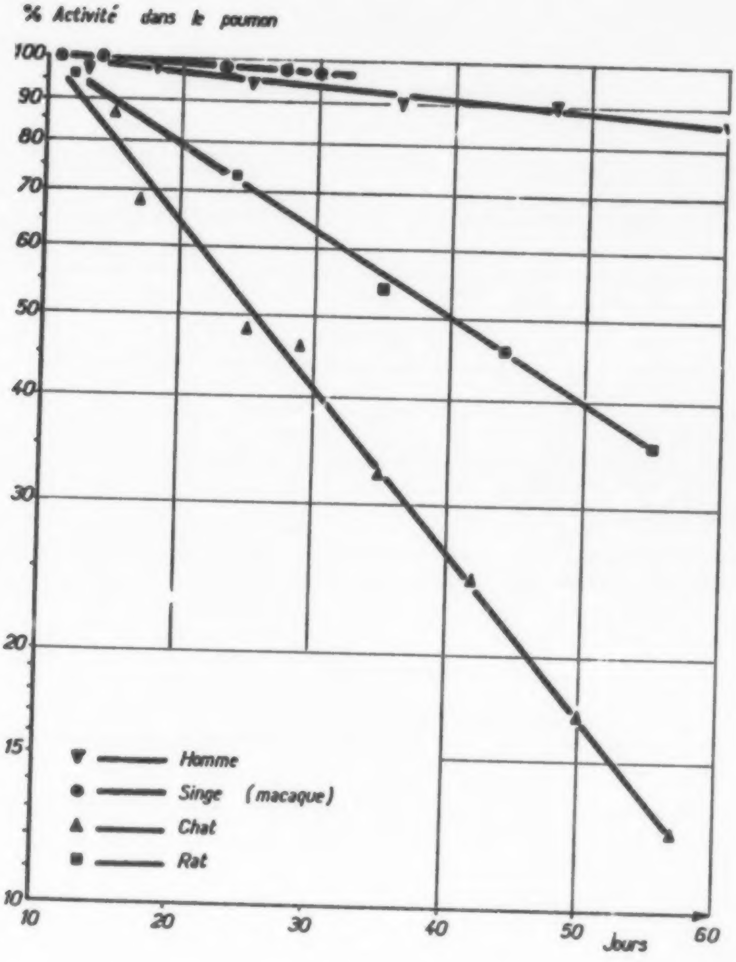

Fig.1 – COURBES D'EPURATION PULMONAIRE HOMME, SINGE (MACAQUE), CHAT, RAT.

de de titane.

4.2 - Polluants gazeux

L'étude, effectuée sur le rat, a porté sur les vapeurs nitreuses et l'anhydride sulfureux. Les résultats indiqués dans le tableau IV représentent les quantités de poussières dosées dans les poumons. Ils montrent que l'inhalation de gaz irritants tend à activer l'épuration pulmonaire. On peut remarquer que l'action de NO_2 est nettement plus marquée que celle de SO_2, malgré une concentration moindre.

Une constatation similaire a été faite avec la fumée de tabac. Bien que les résultats soient encore peu nombreux dans ce domaine, une accélération de l'épuration alvéolaire paraît également se manifester chez l'homme sous l'action de la fumée de tabac, probablement liée à la présence de gaz irritants tels que l'acroléine. Dans le tableau II, les périodes courtes correspondent en effet à trois sujets fumeurs (L..., B..., S...), tandis que les périodes longues correspondent à deux sujets n'ayant jamais fumé (M...) ou ayant cessé de fumer depuis plus d'un an (H...).

5. Conclusion

L'épuration pulmonaire des polluants particulaires est un phénomène sujet à des variations individuelles importantes, tout au moins au niveau alvéolaire. Elle diffère selon la nature du polluant inhalé et est affectée par la quantité de poussières déjà déposée dans les poumons. Audessus d'une certaine charge coniotique, la restauration de la fonction épuratrice est lente et paraît même dans certains cas définitivement compromise. Les vapeurs irritantes tendent à activer légèrement l'épuration alvéolaire selon un mécanisme encore inexpliqué.

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EXEMPLE DE RECHERCHE DANS UNE ATMOSPHERE D'UNE SUBSTANCE CHIMIQUE CAUSE D'EFFETS PATHOLOGIQUES

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RESUME

Le dépistage des problèmes toxicologiques qui peuvent se présenter en entreprise nécessite un dispositif sûr et éprouvé. Nous décrivons une méthodologie d'action à propos d'une intervention type de l'I.N.R.S. dans l'industrie de l'emballage plastique où est apparue une pathologie professionnelle.

Ce dispositif est très progressif: chaque niveau d'action n'est engagé que dans la mesure où le précédent n'a pu apporter de solution au problème soulevé. Il comprend:

- *des équipes d'observateurs locaux spécialisés et sensibilisés aux problèmes d'hygiène industrielle,*
- *une infrastructure destinée à recueillir et transmettre l'information jusqu'aux laboratoires d'analyses et de recherches où elle pourra être traitée,*
- *des équipes pluridisciplinaires, chargées d'étudier l'importance et les implications du problème, ainsi que de généraliser, s'il y a lieu, l'observation fortuite et locale qui a été faite,*
- *des laboratoires de chimie spécialisés dans le prélèvement et l'analyse des substances industrielles présentes dans les atmosphères de travail,*
- *des laboratoires de toxicologie expérimentale, capables:*

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-- *de conduire des études raisonnées sur l'animal, études destinées à fournir au préventeur des moyens de dépistage spécifiques et précoces,*
-- *de pratiquer, sur des échantillons humains, les analyses biologiques correspondantes;*
- *un groupe de travail au sein duquel médecins, toxicologues et statisticiens peuvent interpréter les résultats acquis au cours des étapes précédentes.*

Lorsque l'affaire est instruite, que des causes ont pu être mises en évidence, le dossier est remis aux autorités compétentes qui pourront prendre les mesures qui s'imposent.

ABSTRACT

To get to the root of the toxicological problems that may arise in industry requires a reliable and tested machinery. We describe the procedure for an INRS type investigation in the plastics packaging industry following the appearance of an occupational disease.

The machinery is progressive: each stage only comes into action if the previous stage has failed to find a solution to the problem. It comprises:

- *local teams of specialist observers versed in the problems of industrial hygiene,*
- *an infrastructure to collect and transmit data to analytical and research laboratories where they can be processed,*
- *multidisciplinary teams called upon to study the extent and implications of the problem, and, if necessary, make generally known the random and local observations that have been made,*
- *chemical laboratories specialising in the sampling and analysis of industrial substances present in working atmospheres,*

- *experimental toxicological laboratories capable:*
  - *of carrying out tests on animals in order to provide the preventer with specific methods of early detection,*
  - *and of carrying out appropriate biological analysis on human samples;*
- *a working party within which physicians, toxicologists, and statisticians can interpret the results obtained during the previous stages.*

When the facts have been ascertained and the causes demonstrated, the report is then sent to the competent authorities so that they can take the necessary steps.

1. Introduction

L'étude proposée ici présente une approche méthodologique du dispositif à mettre en place lorsque le problème de rapporter à une cause chimique des troubles observés dans l'industrie se trouve posé.
Ce dispositif fait intervenir différents organismes au service de la prévention : Médecine du travail, Caisses Nationale et Régionales d'Assurance Maladie, Institut National de Recherche et de Sécurité, entr'autres.
Il ne nous appartient pas de fixer le rôle des organismes avec lesquels nous collaborons. Nous nous contenterons de nous situer par rapport à eux dans cette approche méthodologique, et de décrire, à propos d'un exemple précis, notre action, telle que nous la concevons.

2. Origine de l'étude

Le médecin du travail d'une importante entreprise constate l'apparition, chez les ouvriers, de troubles en rapport avec la fabrication des bouteilles en matière plastique. Les troubles en cause consistent principalement en affections sanguines. La médecine du travail, les Caisses Nationale et Régionales sont alertées. La Caisse Nationale charge l'I.N.R.S d'entreprendre une enquête, dans le but de préciser la cause des incidents observés.

3. Recherche d'un constituant de la matière première de ces bouteilles pouvant avoir une action nocive

Un certain nombre de substances chimiques étant connues pour pouvoir être à l'origine des manifestations observées, il importait de vérifier leur présence et leur teneur éventuelle dans l'atmosphère des lieux de travail ainsi que celles de leurs métabolites dans les milieux biologiques.
Par ailleurs, une enquête similaire devait être lancée auprès des entreprises voisines par leur activité.
Cette première intervention apporte les informations suivantes :

Aucun des produits reconnus capables d'entraîner des affections hématologiques de la nature de celles qui ont été décrites n'est présent à une concentration suffisante dans les atmosphères des lieux de travail. Cette constatation est corroborée par le fait que la dégradation thermique des matières premières ne conduit pas, aux températures de mise en oeuvre, à la libération des produits suspects, produits dont les métabolites ne sont d'ailleurs pas retrouvés dans les milieux biologiques ;

Il y a similitude des faits observés dans plusieurs entreprises mettant en oeuvre du chlorure de polyvinyle pour le conditionnement de denrées alimentaires.

Le problème posé existe donc réellement, mais sa cause ne peut être rapportée à aucune des substances connues pour produire ces effets. Une deuxième intervention est décidée.

4. Mise en évidence de la substance probablement responsable

Un inventaire soigneux des corps chimiques présents est dressé. L'un des corps, l'α-phénylindole, paraît suspect. Il est en effet présent dans l'atmosphère, à une concentration non négligeable, et sa toxicité est mal connue. Son étude est alors confiée au laboratoire de toxicologie industrielle expérimentale de l'I.N.R.S.

5. Expérimentation animale

Trois types d'expérimentations sont envisagés :

- l'α-phénylindole est administré par inhalation chez le lapin, et par voies intrapéritonéale et orale chez le rat et la souris. Des examens pharmacodynamiques, hématologiques, anatomopathologiques et biochimiques sont réalisés chez ces animaux intoxiqués en aiguë ;
- l'effet de l'α-phénylindole in vitro, sur une culture de cellules Hela, a été recherché ;
- une étude métabolique préliminaire est effectuée sur le rat.

Ces premiers éléments de recherche ont mis en évidence, chez l'animal, deux substances présentes à un taux anormal dans les urines.

6. Retour à l'observation sur l'homme, accompagnée de traitements statistiques.

L'expérimentation animale ayant établi la corrélation entre l'administration d'α-phénylindole et la sortie urinaire de métabolites anormaux, ceux-ci ont été recherchés systématiquement sur un échantillon d'environ mille travailleurs, appartenant à différentes entreprises, exposés ou non, avant et après poste. Statistiquement, ces analyses ont établi, chez l'homme, la présence des mêmes métabolites, également à des taux anormaux. Des différences significatives ont pu être mises en évidence entre les diverses catégories de travailleurs soumis à investigation.

7. Diffusion de l'information

Le dossier complet de cette recherche préliminaire a été largement diffusé, d'une part vers les milieux responsables, d'autre part vers les utilisateurs, afin que les mesures visant à soustraire les ouvriers à l'inhalation d'α-phénylindole soient prises sans délai.

8. Conclusion

La mise en oeuvre de ce dispositif, appliqué à l'évaluation des effets constatés sur la santé à la suite d'une exposition à un polluant présent dans l'environnement des lieux de travail, présente l'intérêt d'être progressive dans l'utilisation des moyens et de pouvoir être stoppée à la fin de chaque étape, si les résultats sont jugés satisfaisants.
La recherche présentée ici met en évidence quatre points importants :

- la nécessaire collaboration entre médecins et laboratoires de recherche,
- le rôle d'équipes spécialisées dans le prélèvement et l'analyse des atmosphères,
- l'utilité du recours à l'expérimentation animale et l'exploration biochimique raisonnée,
- la nécessité d'un traitement statistique des données acquises.

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UMWELTMESSUNGEN

ENVIRONMENTAL MEASUREMENTS

MESURES DANS L'ENVIRONNEMENT

MISURE AMBIENTALI

METINGEN IN HET MILIEU

ASPECTS OF POLLUTION IN THREE URBAN-CENTRE SITUATIONS IN GREAT BRITAIN

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ABSTRACT

This paper provides an introduction to the automatic pollution monitoring activities carried out by Warren Spring Laboratory. A number of pollutants are studied using some of the latest instrumental methods. Methods of calibration and some experimental findings are discussed relating to general urban and traffic pollution monitoring.

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1. Introduction

Monitoring of roadside pollution in European cities has extended greatly since the 1960s. No longer is concern concentrated only on smoke, carcinogenics, carbon monoxide or even lead. With the seemingly inevitable rise in vehicle population it has become more important to assess the urban situation with respect to a range of primary and secondary pollutants, to examine not only the diurnal pattern of concentrations but also the atmospheric reactions, particularly those induced by sunlight. This has been made possible by the appearance of new instruments which, though sophisticated, can be successfully operated in a continuous mode to provide a detailed account of what is happening in the air.

In the UK we have chosen to make measurements for a period of up to five years in the streets of five cities. Each city has a site in a busy and/or poorly ventilated street. The results and trends should show the intensity of roadside pollution and any effects of traffic flow or legislation on vehicle emissions or fuel composition. Already analysis of the results shows the extent to which London experiences photo-chemical phenomenon. These urban measurements are linked to others in widely scattered rural sites since the time scale of these atmospheric reactions is such that they are not confined to the urban areas where the primary pollutants largely originate.

2. Experimental Methods

2.1 Table 1 summarises the methods routinely used in our survey together with their calibration techniques. Not all these methods are operated simultaneously at all sites in the survey but a minimum of total particulates, particulate lead, carbon monoxide and total hydrocarbons are measured at all sites. Further parameters are measured, and these include wind speed, wind direction, total solar radiation, visual range and traffic count where appropriate.

2.2 Each sensor or instrument is allocated to a particular channel of a 10-channel scanning digital voltmeter with punched paper tape output. This paper tape is then processed centrally by computer. The data acquisition system scans each sensor at five minute intervals with computer integration of the observations to yield hourly mean values. The data are stored on magnetic tape files and are compared on a regular basis with published national and international air quality standards and

TABLE 1. A Summary of the Instrumental Methods and their Calibration

Pollutant	Instrumental method	Absolute calibration method
Carbon monoxide	Non-dispersive infra-red chromatography/flame ionisation	Gravimetric standard gas mixture
Total hydrocarbons	Flame ionisation	Gravimetric standard gas mixture
Oxides of nitrogen	Chemiluminescence	NO_2 permeation tube
Ozone	Chemiluminescence	Neutral potassium iodide method
Sulphur dioxide	Coulometry, conductimetry, flame photometry	West-Gaeke method
Particulate lead	Filter paper collection + XRF analysis	Atomic absorption spectroscopy
Total particulates	Smoke stain reflectivity	
Analysed hydrocarbons	Chromatography/flame ionisation	Gravimetric standard gas mixture

targets.

2.3 The instruments are inspected for malfunction twice weekly and are recalibrated on a weekly basis. The routine calibration procedure involves simpler experimental techniques which are more suited to field operation. The more rigorous absolute calibration procedures listed in Table 1 are reserved for establishing methods and validation of the routine calibration procedures.

3. Some Aspects of the Results for Central London

3.1 A background site was established in Central London above a courtyard so that it would sample the general level of urban pollution in the city and not be specifically influenced by either traffic or local fixed source emissions.

3.2 The computer results are used to calculate the daily, monthly and yearly air quality parameters. Seasonal effects are clearly evident in the air quality values with total particulates, ozone, nitric oxide and carbon monoxide showing relatively simple seasonal dependences.

3.3 Cumulative frequency distributions are particularly useful for summarising air quality data. The range of the data and the time above threshold values can be readily assessed from these distributions. Most of the pollutants being studied showed log-normal cumulative frequency distributions for the daily air quality parameters, daily mean and maximum hourly mean for the day. Notably, nitric oxide, sulphur dioxide, smoke and methane show exceptionally good log-normal distributions. Carbon monoxide, total hydrocarbons, and nitrogen dioxide show deviations from log-normality at low concentrations. Such deviations are accounted for by instrument sensitivity, natural background methane and oxides of nitrogen respectively. Ozone shows large deviations from log-normality over wide concentration ranges.

3.4 The pollutants which are typically associated with motor vehicles and are emitted at street level with poor dispersion behave as area sources in the general urban environment. The pollutants carbon monoxide, hydrocarbons appear with relatively low geometric standard deviations. Sulphur dioxide, which is associated with fixed source combustion, has a much greater geometric standard deviation than for the area source pollutants. Methane which is predominantly a natural background species with some pollution contribution from mans activities, shows the smallest geometric standard deviation of all the air pollutants studied.

3.5 The logarithm of maximum concentration showed a linear relationship with the logarithm of the averaging period for a number of pollutants. This relationship was found to be useful for extrapolating to averaging times not easily or directly assessible from the data itself.

3.6 Elevated ozone concentrations have been measured in Central London during warm, sunny spells during the months of April to September inclusive. The highest hourly mean ozone concentration reached during 1973 was 0.136 ppm with the levels elevated over 0.1 ppm usually for several hours on each occasion. The origin of these elevated ozone concentrations is clearly photochemical and is strongly related to meteorological conditions. During winter months, the ozone concentrations are much lower and show an opposite dependence on meteorological conditions. Only on days with strong winds do ozone concentrations significantly exceed 0.01 ppm.

4. Some Aspects of the Results for Kerbside Sites

4.1 Monitoring sites have been established in heavily-trafficked streets, one in each of London, Cardiff, Glasgow and Birmingham. The air is sampled at a height of two metres, half a metre in from the kerb and is pumped to the instruments for analysis in situ. Simultaneous measurements of wind and counts of vehicles passing the sampling point are also made.

4.2 The pollutants carbon monoxide, total hydrocarbons, particulate lead, total particulates and nitric oxide follow the traffic flow very closely at all times of the day. During the early hours of the morning the traffic flows and pollutant concentrations fall to low values. The correlations between hourly traffic flow and pollutant concentrations for each day are usually highly statistically significant, ($\rho > 0.9$, $N = 24$). These correlations are affected by the wind. This effect is not generally noticeable on an hourly basis due to 'noise' in the pollution emission rate, but is noticeable on a daily basis. With increasing wind speed, the ratio of carbon monoxide to traffic flow decreases significantly on a day-to-day basis.

4.3 The amount of pollution per vehicle flow appears to be heavily dependent on street geometry when comparing different sites. Such variables as 1. the height of buildings on both sides of the street,

2. traffic flow; unidirectional or bidirectional,

3. on which side of the street measurements are made,

and 4. the proximity of intersections, traffic lights, all appear to influence the pollution vs traffic flow correlations.

4.4 The crosscorrelations between the pollutants listed in paragraph 4.2 are also well-characterized on an hourly basis. Sulphur dioxide, provides a contrast for example, and does not correlate well with these other pollutants. Since motor vehicles provide only a small contribution to total emissions of sulphur dioxide, these observations are relatively easy to explain.

4.5 The ratios between the other pollutants have been obtained for canyon streets near to city centres. Generally our ratios agree reasonably well with other published surveys. Further sites are planned, for example to provide information on the influence of the street gradient on these inter-pollutant correlations.

ETUDE DE LA CONTAMINATION DE FOURRAGES ET LEGUMES PAR LE PLOMB ET LES METAUX LOURDS

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RESUME

Les auteurs décrivent la méthode qu'ils appliquent dans l'étude de la contamination de l'environnement et de la chaîne alimentaire par les métaux lourds, et tout particulièrement par le plomb, le cadmium et le zinc.

Une première phase consiste à prélever en sites industriels et urbains, ainsi qu'à proximité des autoroutes, des échantillons de sol ainsi que certains végétaux très répandus dont Plantago major L. (plantain majeur), Ligustrum sp. (troène), Trifolium repens L. (trèfle rampant) et Tussilago farfara L. (tussilage). Les concentrations en éléments métalliques de ces échantillons sont déterminés par oscillopolarographie à tension imposée.

On délimite ainsi des zones à risques accrus où des prélèvements systématiques de fourrages, légumes et fruits sont faits tout au long de la période de végétation. L'évolution et l'importance des retombées en Zn, Cd, Pb, Ni, Co et Cu sont suivies dans ces potagers et vergers de la vallée mosane, à proximité d'usines traitant des minerais. Les résultats sont comparés à ceux obtenus dans la banlieue de Bruxelles, près d'échangeurs autoroutiers et en zone témoin, éloignée de toute source de pollution. Ces résultats font apparaître des risques importants

d'intoxication chronique des hommes et animaux consommant les végétaux contaminés. Parallèlement, des essais portant sur l'absorption, la rétention et la toxicité de ces éléments métalliques, chez les plantes, sont menés en laboratoire. Les résultats acquis, à l'aide de Pb stable et de ^{210}Pb chez Zea mays L. (maïs) sont discutés.

Enfin, des essais d'affouragement de vaches laitières à l'aide de fourrages artificiellement enrichis en Pb stable et ^{210}Pb sont en cours. Ils ont pour but de calculer le taux de transfert du Pb alimentaire dans le lait, les urines et les matières fécales.

La discussion des résultats fait apparaître les risques de contamination de la chaîne alimentaire.

ABSTRACT

Description of the methods used by the authors for their study of contamination of the environment and of the food chain by heavy metals, with particular reference to lead, cadmium and zinc.

The first phase consists of taking samples, in industrial and urban areas and in the vicinity of motorways of soil and various common plants including Plantago major L. (greater plantain), Ligustrum sp. (privet), Trifolium repens L. (white clover) and Tussilago farfara L. (coltsfoot). Concentrations of metal substances in these samples are measured by means of oscillopolarography at a set voltage.

Risk areas are thus demarcated where fodder, vegetable and fruit samples are taken regularly throughout the vegetation period. A watch is kept on the progress and extent of Zn, Cd, Pb, Ni, Co and Cu fall-out in kitchen gardens and orchards in the

vicinity of ore dressing works in the Meuse valley. The results are compared with those obtained in the suburbs of Brussels near motorway intersections and in a control area, away from any source of pollution. These results reveal that there is a serious risk of chronic poisoning in human beings and animals which feed on contaminated plants. Parallel laboratory tests are being carried out on the absorption, retention and toxicity of these metal substances in plants. The results obtained using stable lead and lead ^{210} in Zea mays L. (maize) are discussed.

Finally, dairy cattle are being experimentally fed on fodder which has been artificially enriched with stable lead and lead ^{210}. The aim is to calculate the rate of alimentary lead transfer to the milk, urine and faeces.

Discussion of the results shows the risks of contamination of the food chain.

1. Introduction

La contamination du milieu et de la chaîne alimentaire par les métaux lourds et tout particulièrement par le Pb, le Zn et le Cd, est une agression contre notre environnement relativement récente, dont les répercussions biologiques ne sont encore qu'imparfaitement connues. Nous décrivons, ci-dessous, la méthode que nous utilisons pour suivre la dissémination des métaux lourds (Pb, Zn, Cd, Cu, Co, Ni, Hg, Mn, etc.) dans l'environnement (air, eaux de surface, sol, végétaux) et leurs voies de transfert dans la chaîne alimentaire (boissons, aliments). D'autres publications décrivent plus en détail les principaux résultats acquis (IMPENS et al. (1),(2),(3), DELCARTE et al. (4)).

2. Techniques

Des prélèvements réguliers d'échantillons sont faits dans tout le pays. Après dessication à l'étuve, les échantillons sont minéralisés par voie humide, puis extraits à l'aide d'une solution chloroformique de dithizone et analysés par oscillopolarographie à tension imposée (NANGNIOT, (5)). Les résultats exprimés en ppm/M.S. (mg/kg de matière sèche), ainsi que toutes les caractéristiques et coordonnées de l'échantillon, sont mis sous forme codée en mémoire d'ordinateur pour être traités statistiquement. Les échantillons témoins, non suspects de pollution, proviennent d'une clairière en forêt (Domaine des Epioux, Lacuisine). Enfin, les essais faisant appel aux radionuclides ont lieu au C.E.N./S.C.K. de Mol.

3. Dispersion du plomb dans l'environnement

Nous suivons la dispersion des particules métalliques à l'aide de plantes-témoins. Celles-ci sont présentes dans toutes les stations. De culture aisée, elles se maintiennent en état de végétation pendant la majeure partie de l'année. Leurs caractéristiques botaniques (port des feuilles, rugosité ou pilosité de l'épiderme, présence d'une cuticule) nous ont fait choisir: *Tussilago farfara* L., *Plantago major* L., *Ligustrum sp.* et *Trifolium repens* L..

Parmi les facteurs qui modifient la dispersion du plomb le long des autoroutes, nous avons fait des observations sur :

- l'éloignement de la voie de circulation,
- les caractéristiques du trafic automobile,
- la date du prélèvement d'échantillons,
- les précipitations et le climat,
- le profil de la route et l'orographie,
- la présence d'écrans.

A l'aide de ces plantes-témoins nous avons pu délimiter des zones à risques accrus, où des prélèvements systématiques de fourrages, de fruits et de légumes sont faits.

4. Présence du Plomb dans les fourrages, plantes industrielles et légumes

Dès le 15 août, la plupart des échantillons d'herbes prélevés dans une zone de 30m de part et d'autre d'une autoroute moyennement fréquentée (25.000 véhicules/16h) ont des concentrations en plomb qui dépassent les 100 ppm/M.S.. La consommation prolongée de ces herbages par de jeunes animaux pourrait être une cause d'intoxication saturnine du bétail. A titre préventif, nous avons préconisé l'élimination des produits de fauchage des engazonnements autoroutiers les plus contaminés.

Des observations similaires ont été faites également sur d'autres plantes fourragères: betterave, luzerne, navet, ainsi que sur les céréales, la chicorée, la pomme de terre et les betteraves sucrières. Fort heureusement, pour ces plantes, les parties entrant dans l'alimentation humaine (grains, tubercules, ou racines) ont des teneurs en plomb très faibles, toujours très inférieures à celles des feuilles et tiges. Ce qui confirmerait que la contamination plombique est essentiellement due à un dépôt superficiel et que l'absorption de ce métal par les racines, même dans un sol très contaminé, est très réduite.

Les résultats analytiques obtenus chez des légumes et des fruits sont moins réconfortants (tableau I). Les légumes foliacés (épinard, salade) ou à épiderme velu (haricot) sont les plus contaminés.

Les risques d'ingestion de quantités de plomb appréciables,par ces légumes, est d'autant plus grand, qu'un lavage énergique (à l'acide chlorydrique 10%) auquel certains légumes ont été soumis, s'est révélé peu efficace pour éliminer les dépôts de plomb.

L'analyse simultanée d'autres métaux sur ces échantillons n'a pas montré de corrélation entre de fortes concentrations en plomb et des teneurs élevées en d'autres polluants métalliques.

Tableau I - Contamination de légumes (potager entre 30 et 35m de distance du Ring Nord de Bruxelles - 1973).

Espèce	23 juil.	20 août	6 sept.	4 oct.	7 nov.
Chou blanc	01	20	9	14	13
Chou rouge	03	52	25	13	8
Chou frisé	--	11	21	41	11
Poireau	03	34	12	22	14
Epinard	--	19	--	--	--

Résultats exprimés en ppm -P,b./M.S.

5. Passage du plomb dans la chaîne alimentaire

L'étude en serre de la contamination foliaire de *Zea mays* L., âgé de un mois, a montré que la presque totalité du plomb déposé sous forme de gouttelettes de $Pb(NO_3)_2$ (marqué par ^{210}Pb), reste localisé dans la zone de dépôt. Moins de 2% sont transportés vers les autres feuilles et organes de la plante. Par ailleurs, les essais d'affouragement de deux vaches laitières, à l'aide de plantes de maïs contenant 2,4 millicurie de $^{210}Pb(NO_3)_2$, sont terminés. Les mesures en cours permettent de calculer le taux du ^{210}Pb dans le lait ainsi que le taux de disponibilité par l'animal du plomb associé à une ration de maïs fourrager consommé en vert. (Tableaux II et III)

6. Présence de métaux lourds chez des légumes cultivés en zone industrielle (Engis)

Nous disposons de parcelles, à distances croissantes d'usines traitant des minerais de zinc. Des prélèvements réguliers de végétaux (légumes et plantes-témoins) et d'échantillons de sol y sont faits.

La grande hétérogénéité des résultats d'analyse des sols est due non seulement à l'éloignement ou à l'orientation par rapport aux sources de pollution mais aussi au bouleversement des terrains tant par l'exploitation industrielle que par les travaux de génie civil.

A proximité des usines, sur les côteaux exposés, la flore s'est considérablement appauvrie, seules quelques espèces résistantes survivent (dont *Agrostis* sp.).

Les végétaux cultivés dans les potagers (à plus de 600 m de l'usine, dans la direction des vents dominants) contiennent d'importantes concentrations en Cu, Cd et Zn. A titre d'exemple nous donnons les résultats analytiques pour certains d'entr'eux (tableau IV). Nous comparons les teneurs en ces métaux de différents organes des plantes (feuilles, tiges, racines) en précisant si les échantillons ont été lavés (à HCl 10%) ou non. Les teneurs en éléments métalliques du sol en contact avec les racines sont également données. Des prélèvements à date différente permettent de suivre l'enrichissement progressif en métaux lourds des organes foliacés soumis aux retombées industrielles. La comparaison de laitues cultivées sous couches vitrées et en plein air permet d'apprécier l'importance quantitative de ces retombées actuelles.

Dans certains cas, nous faisons subir à ces légumes contaminés un traitement correspondant aux préparations culinaires normales (épluchage, lavage, cuisson). Les différentes fractions sont analysées séparément. Si une partie des éléments métalliques se retrouve dans l'eau de cuisson, les concentrations en Cu, Cd, et Zn dans les tissus consommés sont encore très élevées: ex. des racines de carotte après épluchage, lavage et cuisson contiennent 30 ppm de Cu, 3 ppm de Cd et 69ppm de Zn (ppm/M.S.).

TABLEAU II

Excrétion (urine,feces) et sécrétion (lait) du ^{210}Pb ingéré avec des tiges de maïs fourrager (vache 36)

Temps écoulé depuis l'ingestion	% dans[x] les feces	% dans[x] l'urine	% dans[x] le lait
1	10,95	$1,5.10^{-3}$	$4,5.10^{-4}$
2	44,16	$7,3.10^{-3}$	$2,7.10^{-3}$
3	28,21	$8,8.10^{-3}$	$3,4.10^{-3}$
4	12,17	$5,5.10^{-3}$	$3,4.10^{-3}$
5	3,89	$4,4.10^{-3}$	$1,9.10^{-3}$
6	1,29	$7,5.10^{-3}$	$1,3.10^{-3}$
7	0,25	$5,2.10^{-3}$	$9,2.10^{-4}$
9	0,02	$1,7.10^{-3}$	$5,2.10^{-4}$
14			$3,3.10^{-4}$
21	$\approx 0,004$	$\leq 2,8.10^{-4}$	$1,0.10^{-4}$
25			$< 6,5.10^{-5}$

[x] pourcentage de l'activité administrée au jour 0.

TABLEAU III

Transfert dans le lait du ^{210}Pb ingéré avec du maïs fourrager (feuilles et tiges).

Forme consommée	Vache N°	Taux[x] de transfert maximum	Temps écoulé depuis l'ingestion (jours).
Feuilles	44	$1,2.10^{-3}$ %	4
Tiges	36	$2,5.10^{-4}$ %	3

[x] pourcentage de la quantité ingérée, secretée par litre de lait.

Tableau IV - Détermination du Cu, Cd, et Zn sur des légumes prélevés à Engis.

			Cu	Cd	Zn
Raphanus sativus	18-V-73	Sol	103	24	10.594
		racine*	9	9	532
		tige *	10	5	728
		feuilles *	40,1	8,9	1.962
	31-X-73	feuilles *	166	16,8	2.354
		feuilles **	257	62,3	3.433
Lactuca sativa	18-V-73 ***	sol	102	20	2.158
		racine *	70	13	1.406
		feuilles *	34	14	421
	18-V-73	sol	80	24	9.612
		racine *	37	20	687
		feuilles *	46	12	5.591
	31-X-73	feuilles *	285	1	961
		feuilles **	295		1.618
Allium porrum	31-X-73	feuilles **	152	7,7	1.275
		feuilles *	54,2	1	294
	15-I-74	feuilles **	7,4	28,9	1.338

Légende : les résultats sont exprimés en ppm/M.S.

* échantillons lavés à HCl 10%

** échantillons non lavés

*** plantes cultivées à l'abri des retombées, sous châssis de verre.

7. Conclusions

Nos observations sur la présence du plomb le long des routes et dans les villes, ainsi que sur la contamination du milieu par les métaux lourds en zone industrielle se poursuivent selon le schéma esquissé ci-dessus.
Les sites "à risques accrus" sont déterminés à l'aide des plantes-témoins. Celles-ci servent aussi d'indicateurs pour suivre l'évolution de la contamination. Les prélèvements réguliers de plantes cultivées permettent l'estimation de la contamination des fourrages et aliments d'origine végétale. L'importance sanitaire de cette contamination est appréciée en étudiant les taux de transfert sol-plante-animal (étape en cours). Si la toxicité de ces métaux est encore peu ou mal connue, ils n'en présentent pas moins un danger potentiel. En attendant la fixation de seuils d'intoxication et de normes admissibles, notre étude se propose de :

- estimer l'importance de la contamination du milieu,
- connaître les voies de transfert du milieu à l'homme,
- guider les recherches épidémiologiques sur les risques d'intoxication de l'homme et des animaux par la chaîne alimentaire.

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EFFECTS OF SECONDARY LEAD SMELTERS ON AIR, SOIL AND VEGETATION QUALITY AND ON LOCAL RESIDENTS IN TORONTO

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ABSTRACT

As part of an interdisciplinary environmental research programme, soils and vegetation around two lead recovery smelters were initially screened for their lead content. Lead accumulation in surface soil had reached ~5% close to one smelter and exceeded 5,000 μg/gram in residential gardens close to both plants. Although this level of contamination may have been caused by past emissions, the lead content of foliage exceeded 1,000 μg/gram close to one smelter, thus suggesting an ongoing pollution problem. The rate of lead accumulation in vegetables, tree saplings and grass turf transplanted into the contaminated area substantiated this conclusion.

While concentrations of suspended lead particles in the atmosphere near the smelters were significantly higher than at an urban control site, the monthly means of 2-5 μg/m^3 were similar to values recorded in downtown areas of other large North American cities. In contrast, the lead in dust-fall was ext-

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remely high, monthly averages being as high as 600-1200 mg/m^2/ 30 days in a residential area close to one smelter. Particle size analysis of the lead aerosol showed the difference to be due to large particles, probably from found-level operations, falling out close to the smelter. The lead-bromine ratios also indicated that localized industrial rather than automobile emissions, were responsible for 75% of the current fallout.

Analysis of lead in blood and hair of residents living within 150 metres of one smelter were compared with an urban control group. The major difference in the data was caused by about 25% of the children sampled having blood lead levels in excess of 40 µg/100 ml and hair values higher than 80 µg/gram. An exponential relationship between lead in hair and blood was established. It appeared that ingestion of contaminated dirt and dusts rather than paint "pica" was the major lead source. Neurological and biochemical abnormalities were recorded in 10% of the children sampled.

As dust-handling rather than stack emissions appeared to be the major source of lead contamination of the neighbourhood it is hoped that secondary smelters in urban areas enclose such operations and buffer zones be established around new secondary smelters.

During the spring of 1973, surface soils and leaves from a variety of tree and grass species were collected from around metalliferous industries located in Toronto in order to determine whether the biological monitoring techniques used by Goodman and Roberts(1) provided a useful tool for identifying areas of elevated metal fallout in a large urban area. An intensive survey of the urban background indicated that leaves of *Poa* and *Acer* species contained less than 100 ppm. lead, and surface soils less than 500 ppm. A number of abnormal concentrations were found in industrial areas but the most significant were around two secondary lead smelters where vegetation and soil samples contained 500 and 8,000 ppm respectively.

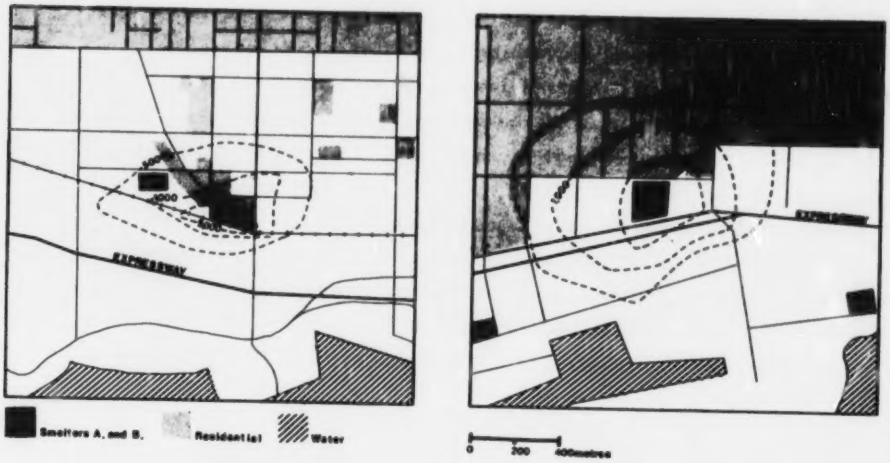

Fig. 1. Lead in surface soil (0-2 cm) around two secondary lead smelters.
Isopleth values are micrograms Pb extracted by hot $HNO_3/HClO_4$ acids per gram air-dry soil.
A = Smelter A B = Smelter B
M.I. = municipal incinerator S.I. = sewage incinerator.

Both smelters are located to the north of an elevated expressway, and close to municipal incinerators with residential housing to the north (Figure 1). Smelter A recycles car batteries whereas Smelter B also processes crude lead oxide. The pollution problems associated with secondary smelters are different from those of primary smelters in that there are fewer guest elements and sulphur in the raw material. Although one would expect a mosaic of elevated lead concentrations in surface soils in an area with such a multiplicity of sources, isopleths constructed from analysis of samples for 150 sites in each area, indicated an exponential decrease with distance from each smelter and with depth in soil. Within 50 metres of the stack of Smelter A lead accumulation in surface soils reached 4-5% and was greater than 1,000 ppm in grass leaves. High soil levels may be caused by past emissions but high metal levels in foliage indicate current contamination (Roberts and Goodman (2)). This conclusion was tested by transplanting saplings of birch *(Betula alba)* and maple *(Acer saccharinum)* into the contaminated area. The rate of lead accumulation was rapid at first, followed by a slower asymptotic phase reaching 1200 ppm for birch and 300 ppm for maple at the time of leaf-fall. 40-60% of the contamination was superficial and could be removed by washing in a 1% detergent solution. Lead retention was greater in the birch leaves, probably because of their greater pubescence and the large size of the stomata. A marked decrease in productivity was noted. The physiological basis of these effects caused by lead deposits is now being investigated.

A number of authors (Graovac-Leposavic et al (3), McIntire and Angle (4) and Stofen (5)) have found significant increases in both daily lead intake and lead body burdens of people living in high exposure conditions close to both primary and secondary lead smelters. As the distance between crushing/smelting operations and the nearest residential area was

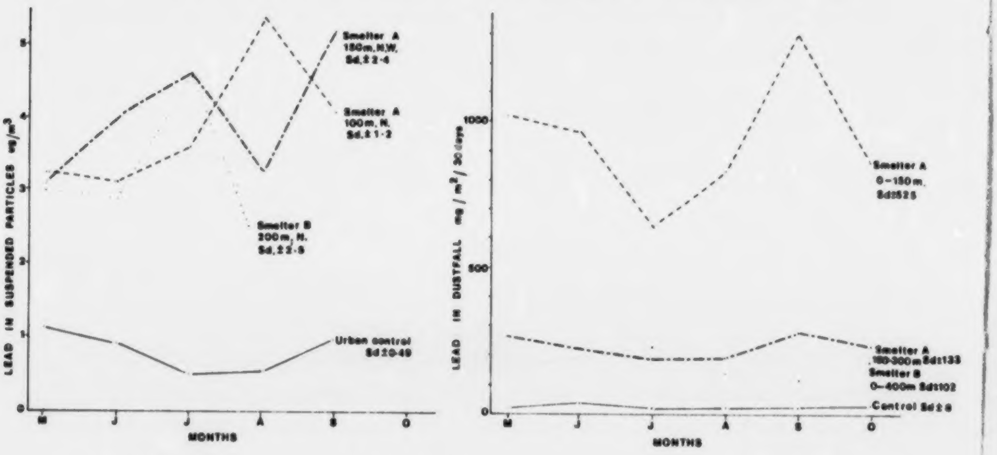

Figure 2. Lead in Suspended Particles and Dustfall Close to Two Secondary Lead Smelters and in an Urban Control Area. Sd = standard deviation of all values recorded in each region.

only 50-100 metres at Smelter A, an extensive survey of lead concentrations in the air, the people and their home environment was instigated. The results have been compared with an urban control group living in similar aged housing.

Monthly arithmetric means of lead concentrations in suspended particles collected over 24-hour periods by high-volume samplers varied between 2 and 5 ug/m^3 close to both smelter A and B compared to 0.45-1.1 ug/m^3 in the control area (Figure 2). The daily values for the smelter site form a log-normal distribution, as values up to 14 ug/m^3 were recorded on days when the wind was from the smelter direction. The smelter and control daily values were subjected to a paired-comparison test and found to be significantly different at the 0.1% level. The mean values around the smelter, although high for Toronto, are not unusually high when compared to downtown areas of large U.S. cities. In marked contrast, lead in dustfall was extremely high - up to 1200 mg/m^2/30 days - compared with less than 35 in the control area. Lead in dustfall also decreased exponentially with distance. The rate of total deposition (cm/sec) obtained by dividing the lead and dustfall by the concentration of suspended particles, was found to be 1-2 for the urban area and increased up to 14 in the vicinity of the smelter. This difference was explained by particle size fractionation of the aerosol using an Andersen Impactor, which indicated that the percentage of particles above 3.3 microns increased from 20% in the urban control area to 70% close to the smelter on episodal days. The mass median diameter of airborne lead on episodal days was 4.6±1.3 microns compared to 0.8±0.2 microns for urban control sites. These large particles were mainly of smelter origin since lead in automobile exhausts is mainly submicron in size. The automobile contribution to total atmospheric lead burden near the refineries was estimated to be about 20% on episodal days using the Br/Pb ratio of the urban area and the bromine concentration by the smelter to calculate the airborne automotive lead. Weslowski found similar changes in Br/Pb ratios around smelters.

The high concentrations of lead in dustfall were of particular concern as Nordman et al (7) found mean blood lead levels increased from 12 to 24 ug/100 ml as lead in dustfall increased from 20 to 200 mg/m^2/30 days close to a secondary lead smelter. Analysis of capillary blood using the method of Cruz and Van Loon (8) from 45 people living in our urban control area gave a mean of 17 ug/100 ml for adults and children - no individuals above 40 ug/100 ml were recorded. This baseline data has since been substantiated in a survey of over 1,000 individuals by the Toronto Board of Health, and is surprising in that it is considerably lower than has been reported for downtown areas of large U.S. cities.

The arithmetic mean for the smelter community was significantly higher than the control group. The mean is skewed, however, by occurrence of a small number of individuals with markedly elevated levels. It is interesting to note that these individuals are usually male and under the age of 14. This observation of an upward shift in the population lead norm was borne out by analysis of hair using the Photon Activation Analysis technique described by Chattopadhyay and Jervis (9). The urban control group had a modal concentration of 17 ppm compared to a range of 20 to 160 ppm in the smelter group. This difference was not due to surface contamination as only 10-20% could be removed by vigorous washing. Correlation of lead in blood and hair from 67 individuals indicated an exponential distribution - values ranging from 10 to 60 ug/100 ml in blood and 3 to 166 ppm in hair - fitting the equation $\log Y=0.7001+0.0277\ X$ ($r=0.798$). A similar correlation has been found by Hammer et al (10) for schoolboys living in smelter and urban areas. This is of considerable interest as individuals exposed to acute doses of lead, where hair and blood lead levels fluctuate widely over short periods, exhibit no such correlation (Kopito et al (11).These observations, together with the finding that lead concentrations do not fluctuate widely in centimetre sections along the hair of children whose blood lead levels are between 40 and 60 ug/100 ml, suggests that their body burden is in equilibrium with the environmental burden. Any further source of intake

TABLE I

PERCENTAGE DISTRIBUTION OF LEAD IN CAPILLARY BLOOD AND HAIR OF PEOPLE LIVING NEAR A SECONDARY LEAD SMELTER AND A CONTROL AREA

			Blood Lead Level (ug/100 ml)						
	n	x	0-9	10-19	20-29	30-39	40-49	50-59	60+
Urban Control	45	17	9	64	22	5	0	0	0
Smelter Area	32	33	0	6.5	25	41	18.5	9	0

			Hair Lead Level (ug/gram)						
	n	x	0-9	10-19	20-29	30-39	40-49	50-99	100+
Urban Control	45	17	27	37	18	18	0	0	0
Smelter Area	51	52	0	22	8	26	16	12	16

x = arithmetic mean

would increase the body burden from this sub-clinical level to levels at which clinical symptoms of lead poisoning may appear.

More extensive blood sampling has since been completed and 16 children, i.e. 2% of those living within 500 metres of both Smelter A and B, have been given Ca EDTA treatment. All children showed lead excretion above baseline levels and 2 achieved more than 600 ug Pb within 24 hours. 7 demonstrated more than 1000 ug ALA in urine per 24 hours. There were 5 cases of hyperactivity and 5 with neurological abnormalities. 3 showed definite lead lines in bone epiphyses. It appears, therefore, that the increased lead absorption, associated with ingestion and inhalation of dirt and dusts in the Toronto situation, does not appear sufficient to cause clear-cut symptoms of poisoning but may cause subclinical metabolic effects.

It would seem that if it is not possible to have buffer zones around secondary lead smelters in urban areas, both ground level and stack emissions will have to be better controlled than is the current practice. In addition, air quality criteria based on the lead content of dustfall as well as suspended lead particles are required to prevent environmental contamination. Levels of 100 mg/m^2/30 days for lead in dustfall and a daily concentration of 5 ug/m^3 or monthly geometric average of 2 ug/m^3 for lead in suspended particles has been suggested for this region.

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SUI VANTAGGI PRESENTATI DALL'USO DELLA FORNACE A GRAFITE COME NUOVA TECNICA DI ASSORBIMENTO ATOMICO NELL'ANALISI DELL'INQUINAMENTO DELL'AMBIENTE DI LAVORO

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RIASSUNTO

Alcuni elementi metallici (Piombo, Zinco, Cadmio, Antimonio, Argento, Rame, Nichel, Cobalto) presenti a livelli di tracce in differenti ambienti di lavoro, sono stati analizzati mediante l'uso della spettroscopia per assorbimento atomico, con le nuove tecniche che utilizzano il fornetto a grafite.

Vengono presi in esame i vantaggi presentati dalle nuove metodiche di dosaggio e di prelievo.

ABSTRACT

Some metallic elements (lead, zinc, cadmium, antimony, silver, copper, nickel, cobalt) of which traces are sometimes found in various types of working environment, were analysed by means of atomic absorption spectroscopy and new techniques based on the use of the graphite furnace.

The paper covers the working conditions, the results obtained and the advantages offered by the new methods of sampling and quantitative analysis which were used.

La determinazione degli inquinanti atmosferici negli ambienti di lavoro rappresenta un parametro importante nella valutazione della salubrità dell'ambiente e deve essere eseguita con la massima precisione possibile data la particolare importanza che ormai viene attribuita alla presenza anche di tracce minime di diversi inquinanti.

Per queste ragioni nel nostro Istituto si è sempre voluto, nel corso degli anni, affinare le varie determinazioni, modificando e migliorando le tecniche operative. Riferiremo, nel corso di questo nostro intervento, sui vantaggi offerti dall'impiego della fornace a grafite per la determinazione abituale di tracce di metalli nell'aria degli ambienti di lavoro. I dati che riportiamo si riferiscono, principalmente, al dosaggio ripetuto di metalli, presenti nell'aria di alcune miniere metallifere della Sardegna, durante diverse fasi della estrazione del minerale.

L'uso di un fornetto a grafite, oltre a permettere di rilevare tracce minime dei vari inquinanti, ci ha dato la possibilità di ripetere su di uno stesso campione la determinazione contemporanea di diversi metalli e, data l'alta sensibilità della suddetta metodica, è stato sufficiente eseguire campionamenti ridotti sia nel volume sia nel tempo.

METODICA

Prelievo dei campioni

Per i prelievi dei campioni d'aria sono state impiegate le seguenti attrezzature:

1) prelevatori automatici Dual e Sequential Sampler (Gelman); prelevatori automatici modello D P 12 (Terzano);
2) contatori registratori (Terzano); contatori a secco (S.I.M. Brunt);
3) portafiltri metallici (Gelman) corredati di membrane Metricel con pori del diametro di 45 micron (Gelman).

I prelievi dei campioni d'aria sono stati effettuati in punti opportunamente studiati, onde poter disporre di un quadro rispecchiante le condizioni generali dell'ambiente di lavoro: gallerie, fronti di avanzamento, coltivazioni, sgombero, fornelli, carreggi, tramogge.

L'aria è stata prelevata a m. 1,50 dal suolo, alla velocità di 1-2 litri al minuto e per 30'-60' per ciascun filtro.

Dosaggio

Per la determinazione dei metalli abbiamo utilizzato uno spettrofotometro per assorbimento atomico mod. 495 (Beckman), corredato di un fornetto a grafite "Massmann Cuvette" (Beckman). Per la introduzione delle piccole quantità di campione sono state adoperate le micropipette Eppendorf Marburg da 10

	Pb		Zn		Cd		Sb		Ag	Cu	Ni	Co
	Max	Min	Max	Min	Max	Min	Max	Min				
a	0,064	0,012	0,090	0,010	0,0010	0,000	0,0007	0,000	0,000	0,000	0,000	0,00
b	0,046	0,008	0,045	0,007	0,0000	0,000	0,0000	0,000	0,000	0,000	0,000	0,00
c	0,062	0,012	0,068	0,005	0,0008	0,000	0,0004	0,000	0,000	0,000	0,000	0,00
d	0,022	0,005	0,031	0,003	0,0001	0,000	0,0011	0,000	0,000	0,000	0,000	0,00
e	0,009	0,003	0,015	0,002	0,0005	0,000	0,0000	0,000	0,000	0,000	0,000	0,00
f	0,028	0,004	0,035	0,003	0,0002	0,000	0,0000	0,000	0,000	0,000	0,000	0,00

a) Miniera di San Giovanni (50 determinazioni)
b) Miniera di "Su Zurfuru" (35 determinazioni) esterno
c) Miniera di "Su Zurfuru" (50 determinazioni) interno
d) Miniera di "Barega" (30 determinazioni)
e) Miniera di "Masua" (20 determinazioni)
f) Miniera di "Mantega" (20 determinazioni)

e 20 microlitri.

Soluzioni standard dei metalli

Sono state adoperate soluzioni acquose dei seguenti metalli: Pb, Zn, Sb, Cd, Cu, Ag, Ni, Co, della ditta BDH, tutte alla concentrazione di 1000 ppm.

Le membrane utilizzate per i prelievi, su cui si era depositato il materiale proveniente dall'aria dei cantieri di lavoro, sono state trattate ripetutamente con aliquote da 5 ml di HNO_3 concentrato "Suprapur" della Ditta Merck, onde mandare in soluzione tutto il materiale residuo;quindi con acqua bidistillata abbiamo portato a volume, in palloncini tarati da 25 ml, le soluzioni ottenute e sulle stesse abbiamo eseguito i dosaggi dei metalli presenti. I metalli sono stati determinati direttamente nelle soluzioni acquose e la loro concentrazione è stata ricavata da una curva di taratura allestita preventivamente. Per valutare più precisamente la concentrazione dei metalli, abbiamo operato anche con il metodo delle aggiunte successive, ed allo stesso modo abbiamo anche controllato le interferenze della presenza contemporanea di diversi metalli.

Ci limitiamo a riportare in tabella dei rilievi eseguiti nelle varie miniere, i valori (in mg/m^3) massimi e minimi, nonchè, per ciascuna miniera, il numero di prelievi eseguiti.

Conclusioni

L'uso del fornetto a grafite nella determinazione quantitativa dei metalli, presenti nell'atmosfera dei vari ambienti di lavoro, ci ha fornito notevoli vantaggi legati soprattutto alla alta sensibilità di questa metodica rispetto ad altre.

Come risulta dalla tabella allegata, con queste tecniche abbiamo ottenuto sia dei risultati più precisi nella determinazione di metalli (come Pb e Zn) presenti a livelli più facilmente rilevabili, sia nel dosaggio delle tracce minime (come Cd e Sb) non altrimenti evidenziabili con altre metodiche. Infatti per la determinazione di queste tracce minime occorrerebbero dei prelievi massivi e prolungati nel tempo, il che potrebbe comportare l'interferenza dei metalli presenti in concentrazioni superiori.

LEVELS OF SOME TRACE ELEMENTS IN BABY AND ADULT DIETS IN ITALY

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ABSTRACT

Cadmium, chromium, copper and zinc have been measured in nearly 60 samples of various infant foods present on the Italian market, including powder milk, strained meats, infant cereals, floure and fruit juices.

Similar measures have been completed in a pool of food samples representing an average adult diet for one week.

The same elements have also been measured in maize, cassava, rice, peanuts, beans, tomatoes, spinach coming from an African region (Dahomey).

From the results, the daily intake for infants and adults has been calculated and compared with data shown in other reports.

1. Introduction

The problems of food contamination by different elements is to be approached, keeping in mind that many of these are the so called "trace elements" whose role in human and animal nutrition is well known since the deficiency of some of them in the diet may induce particular syndromes of malnutrition.

At present the nutritional requirements of all the elements found in the human body, are not yet known.

Actually the trace elements can be divided into three groups (1) the essential ones, the probable essentials, and the non essentials.

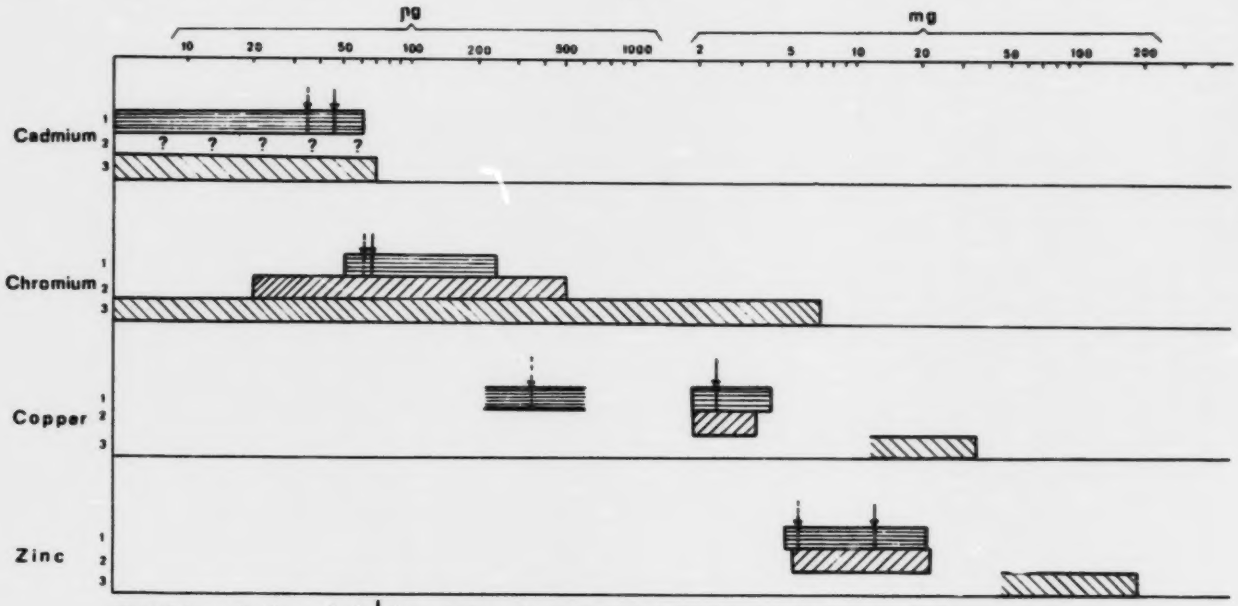
Ten trace elements considered essential nowadays are: iron, iodine, copper, zinc, manganese, cobalt, molybdenum, selenium, chromium, and tin. Among the trace elements of which there is no certainty as to their essentiality, are: nichel, fluorine, bromine, arsenic, vanadium, cadmium, barium and strontium. Furthermore, a certain number of trace elements (between 20 and 30) though found in different body tissues, do not meet with the criteria established by Cotzias (2), to be regarded as essentials.

1. - The criteria are: Presence in healthy tissues of all living beings;
2. - Approximate constant concentration in different species;
3. - Biochemical, functional and structural abnormalities induced by the deficiency of an element in the diet;
4. - Reverse of these abnormalities after the addition of the deficient element to the diet.

The non essential elements are believed to reach the human body trough environmental contamination and, in confirmation of such an hypothesis, attention is drawn to the different distributing pattern on the concentration of essential and non essential trace elements in the human organs: for the essential ones normal idstribution has been noted, whereas the non essential elements have a log-normal distribution.

Daily intakes of Cd, Cr, Cu and Zn

Figure 1



Results of the present work { (↓) = daily intake in infants at the end of first year
(↓) = " " " adults

1) Actual intakes

2) Recommended intakes

3) Maximum allowable daily intakes

(values have been calculated from the current litterature and in particular from oligoelements in human nutrition - OMS Sez. Rapp. Techn. 1973 - 532)

Cadmium, is among the elements that present this last behaviour but, for other reasons, it is thought to be essential.

Finally it should be emphasized that for some elements the levels which can give rise to accumulation and toxicosis are not far from the nutritional requirements (3-4-5).

2. Methods

Starting from the above consideration four elements have been measured: three essential, chromium, copper and zinc and one probable essential, cadmium, in the following items:

a) infant foods, sold on the Italian market (table I);
b) samples of infant formula milk produced from 1952 to 1966;
c) dishes of an average diet for adults, sampled for one week and pooled before analysis;
d) a certain number of foods sampled in an African area (Dahomey).

TABLE I Infant food types analysed.

Food	No producer	No products
1 Milk powder	7	17
2 Infant flours	7	14
3 Strained meats	4	8
4 Strained fruits	5	9
5 Fruit juices	4	7

Apparatus:

The atomic absorption spectrophotometer used in this research was a Jarrel-Ash-Atomsorb.

Procedure:

50 g. of the sample was ashed at 400°C then dissolved in concentrated HNO_3 and left in a muffle furnace until the ashes became completely white. The ashes were added with HCl (1:1) then heated, filtered, transferred to 25 ml. volumetric flask and diluited with distilled water to the mark.

All the samples were then measured by the additioning me method. The performance of the analysis was tested by determining the recoveries of Cd. - Cr. - Cu. and zinc.

Therefore known amounts of Cd, Cu, Cr, and zinc were added to 50 g. of each sample, the samples were then processed by a procedure already described (6).

Analyses on fifteen replicated samples indicated recoveries as follows: 71,0 ± 5,7% Cd, 100 ± 3,2% Cu, 99,1 ± 2,7% Cr, 100,1 ± 3,4% Zn.

The reproducibility of the analyses has been determined by analysing each sample three times therefore calculating the standard deviation.

3. Results and Discussion

The results concerning infant foods measured are shown in tables II, III, IV, V, VI and VII. Each figure is followed by twice the standard deviation.

No evidence has been found of a rise in the levels of Cd, Cr, Cu, and of zinc in infant milk produced from 1952 onward. On the basis of the average values in the examined foods the daily intake of the four elements has been calculated (table VIII according to the food consumption data in the 1st year of life (7).

Table IX shows the daily intakes of Cd, Cr, Cu and Zn in adults with average adult diet.

In figure 1 a comparison has been made between the daily intake concerning infants and adults found in the present research work and those reported in other surveys; the maximum non toxic levels, as far as they are known, have also been indicated. From figure 1 it can be seen that the daily cadmium intake is very near the maximum allowed level, indicated by the WHO expert committee in 1973.

It is also evident that at the end of the 1st year of life the intake of cadmium and chromium are very near to the adult level. The results of the measurements of Cd, Cr, Cu and Zn in some African food samples are shown in table 10.

TABLE II

Cadmium, Chromium, Copper and Zinc in infant formula milk.
(The values are followed by twice the standard deviation).

Samples n°	Cd p.p.m.	Cr. p.p.m.	Cu. p.p.m.	Zn p.p.m.
1	0,20 ± 0,01	0,29 ± 0,02	0,79 ± 0,12	18,6 ± 4,6
2	0,23 ± 0,02	0,32 ± 0,02	0,77 ± 0,06	23,3 ± 0,5
3	0,24 ± 0,03	0,27 ± 0,03	0,69 ± 0,03	15,5 ± 1,4
4	0,21 ± 0,02	0,30 ± 0,04	0,47 ± 0,06	23,5 ± 0,6
5	0,23 ± 0,01	0,28 ± 0,02	0,70 ± 0,04	23,6 ± 1,2
6	0,24 ± 0,02	0,28 ± 0,02	0,64 ± 0,03	11,4 ± 1,6
7	0,21 ± 0,03	0,27 ± 0,03	0,53 ± 0,04	27,3 ± 3,2
8	0,21 ± 0,03	0,28 ± 0,05	0,97 ± 0,06	24,4 ± 1,7
9	0,22 ± 0,02	0,29 ± 0,03	0,50 ± 0,05	25,6 ± 2,1
10	0,14 ± 0,01	0,23 ± 0,03	0,26 ± 0,02	9,7 ± 0,6
11	0,18 ± 0,02	0,23 ± 0,03	0,37 ± 0,02	19,2 ± 2,1
12	0,23 ± 0,02	0,27 ± 0,02	0,35 ± 0,05	22,2 ± 3,8
13	0,20 ± 0,02	0,31 ± 0,04	0,53 ± 0,03	24,2 ± 3,4
14	0,24 ± 0,02	0,29 ± 0,03	0,46 ± 0,05	20,5 ± 1,4
15	0,23 ± 0,04	0,37 ± 0,02	0,73 ± 0,04	24,2 ± 3,4
16	0,23 ± 0,02	0,37 ± 0,04	0,67 ± 0,10	23,5 ± 2,1
Average	0,21 ± 0,05	0,29 ± 0,08	0,58 ± 0,36	21,0 ± 10

TABLE III

Cadmium, Chromium, Copper and Zinc in infant formula milk produced from 1952 to 1966. (The values are followed by twice the standard deviation).

Samples	Cd. p.p.m.	Cr. p.p.m.	Cu p.p.m.	Zn. p.p.m.
1952	0,20 ± 0,01	0,34 ± 0,03	1,0 ± 0,14	21,0 ± 0,5
1954	0,21 ± 0,02	0,31 ± 0,04	0,87 ± 0,04	23,2 ± 0,7
1955	0,24 ± 0,02	0,33 ± 0,02	0,81 ± 0,05	25,0 ± 1,4
1956	0,21 ± 0,01	0,32 ± 0,02	0,73 ± 0,2	19,7 ± 1,0
1957	0,23 ± 0,03	0,36 ± 0,04	0,68 ± 0,07	24,6 ± 1,6
1958	0,22 ± 0,02	0,33 ± 0,02	0,78 ± 0,04	22,5 ± 1,4
1959	0,21 ± 0,02	0,36 ± 0,04	0,80 ± 0,02	23,2 ± 0,7
1960	0,22 ± 0,02	0,37 ± 0,03	0,77 ± 0,07	24,8 ± 2,2
1963	0,21 ± 0,02	0,31 ± 0,04	0,83 ± 0,08	22,5 ± 1,4
1963	0,21 ± 0,02	0,33 ± 0,02	0,68 ± 0,05	21;5 ± 1,4
1964	0,21 ± 0,03	0,30 ± 0,02	0,69 ± 0,08	22,2 ± 0,7
1965	0,20 ± 0,02	0,31 ± 0,04	0,67 ± 0,03	21,6 ± 1,4
1965	0,21 ± 0,03	0,30 ± 0,07	0,67 ± 0,05	22,3 ± 0,5
1966	0,21 ± 0,02	0,30 ± 0,02	0,63 ± 0,05	24,7 ± 0,7
1966	0,21 ± 0,02	0,31 ± 0,04	0,64 ± 0,10	26,2 ± 2,0
Average	0,21 ± 0,03	0,32 ± 0,04	0,74 ± 0,20	23,0 ± 3,4

TABLE IV

Cadmium, Chromium, Copper and Zinc in baby foods (strained meats).
(The values are followed by twice the standars deviation).

Samples	Cd. p.p.m.	Cr. p.p.m.	Cu p.p.m.	Zn p.p.m.
1	0,04 ± 0,005	0,20 ± 0,01	1,2 ± 0,07	20,0± 1,3
2	0,04 ± 0,005	0,23 ± 0,01	1,1 ± 0,07	19,0± 1,3
3	0,03 ± 0,004	0,21 ± 0,01	1,3 ± 0,08	35,0± 2,4
4	0,05 ± 0,007	0,28 ± 0,02	1,1 ± 0,07	38,0± 2,5
5	0,07 ± 0,008	0,22 ± 0,02	0,8 ± 0,05	11,0± 0,7
6	0,03 ± 0,004	0,10 ± 0,005	0,4 ± 0,02	16,6± 1,1
7	0,02 ± 0,003	0,10 ± 0,005	0,4 ± 0,02	16,2± 1,1
8	0,05 ± 0,006	0,10 ± 0,005	0,4 ± 0,02	22,8± 1,5
Average	0,04 ± 0,03	0,13 ± 0,14	0,8 ± 0,7	22 ± 18

TABLE V - VI

Cadmium, Chromium, Copper and Zinc in baby foods (A - fruit juices, B - strained fruits).
(The values are followed by twice the standard deviation).

A

Samples	Cd. p.p.m.	Cr p.p.m.	Cu p.p.m.	Zn. p.p.m.
1	< 0,01	0,04	0,34 ± 0,04	0,95 ± 0,1
2	< 0,01	0,04 ± 0,01	0,10 ± 0,02	0,76 ± 0,1
3	0,01	0,04 ± 0,01	0,30 ± 0,03	0,95 ± 0,1
4	0,01	0,04 ± 0,01	0,30 ± 0,01	0,57 ± 0,2
5	0,01	< 0,001	0,27 ± 0,02	0,95 ± 0,2
6	0,01	0,04 ± 0,01	0,29 ± 0,03	0,91 ± 0,1
7	0,01	0,07 ± 0,01	0,50 ± 0,03	1,33 ± 0,1
Average	0,01	0,04 ± 0,04	0,29 ± 0,22	0,92 ± 0,44

B

1	0,02	0,05 ± 0,01	0,6 ± 0,2	3,3 ± 0,5
2	0,02	0,12 ± 0,02	1,5 ± 0,2	3,3 ± 0,4
3	0,02	0,10 ± 0,02	0,87 ± 0,3	3,5 ± 0,3
4	0,02	0,12 ± 0,03	0,91 ± 0,2	3,3 ± 0,4
5	0,02	0,91 ± 0,10	0,65 ± 0,2	1,8 ± 0,3
6	0,02	< 0,01	0,37 ± 0,2	1,8 ± 0,4
7	0,02	0,07 ± 0,02	1,05 ± 0,3	3,0 ± 0,5
8	0,01	0,04 ± 0,01	0,61 ± 0,3	2,6 ± 0,3
9	0,01	0,04 ± 0,01	0,39 ± 0,1	1,3 ± 0,3
Average	0,02	0,16 ± 0,56	0,76 ± 0,72	2,7 ± 1,5

TABLE VII

Cadmium, Chromium, Copper and Zinc in infant flours. (The values are followed by twice the standard deviation).

Samples n°	Cd. p.p.m.	Cr. p.p.m.	Cu. p.p.m.	Zn p.p.m.
1	0,21 ± 0,03	0,22 ± 0,07	4,7 ± 0,3	23,0 ± 1,4
2	0,18 ± 0,03	0,09 ± 0,02	1,7 ± 0,1	11,5 ± 2,8
3	0,12 ± 0,02	0,16 ± 0,02	2,5 ± 0,1	15,3 ± 2,2
4	0,21 ± 0,03	0,17 ± 0,03	1,3 ± 0,3	12,5 ± 2,8
5	0,22 ± 0,01	0,42 ± 0,07	6,8 ± 0,5	25,5 ± 3,4
6	0,11 ± 0,01	0,23 ± 0,03	3,9 ± 0,4	17,3 ± 2,4
7	0,18 ± 0,05	0,09 ± 0,01	5,0 ± 0,3	20,0 ± 2,8
8	0,10 ± 0,01	0,05 ± 0,01	1,2 ± 0,1	11,2 ± 0,7
9	0,20 ± 0,02	0,26 ± 0,05	0,9 ± 0,1	11,7 ± 0,7
10	0,18 ± 0,03	0,31 ± 0,03	2,5 ± 0,1	18,2 ± 2,0
11	0,05 ± 0,01	0,03 ± 0,01	2,5 ± 0,3	12,5 ± 1,4
12	0,22 ± 0,03	0,49 ± 0,03	2,5 ± 0,1	12,5 ± 0,28
13	0,18 ± 0,02	1,4 ± 0,20	1,7 ± 0,2	15,0 ± 1,0
14	0,16 ± 0,02	0,13 ± 0,04	7,4 ± 0,4	15,5 ± 1,4
Average	0,16 ± 0,08	0,22 ± 0,68	3,2 ± 4,0	15,4 ± 2,2

TABLE VIII

Daily intake of Cadmium, Chromium, Copper and Zinc from 4th. month to 12thmonth of life.

	gr.	Cd (µg)	Cr (µg)	Cu (µg)	Zn. (mg)
4th. month					
milk	640	21,0 (14-24)	29,1 (22-39)	58,9 (25-103)	2,1 (0,9-2,9)
flours	15	2,4 (0,7-3,3)	3,3 (0,4-21)	48,0 (13-111)	0,2 (0,2-0,4)
meat	30	1,2 (0,9-2,1)	4,8 (3-8,4)	24,0 (12-39)	0,6 (0,3-1,0)
Total		24,6 (15-30)	37,1 (25-68)	131,0 (50-253)	3,0 (1,4-4,4)
5th. month					
milk	640	21,0 (14-24)	29,1 (22-39)	58,9 (25-103)	2,1 (0,9-2,9)
flours	25	4,0 (1,2-5,5)	5,5 (0,7-35)	80,0 (22-185)	0,4 (0,3-0,6)
meat	100	4,0 (3-7)	16,0 (10-28)	80,0 (40-130)	2,2 (1,1-3,8)
Total		29,0 (18-36,5)	50,0 (33-102)	219,0 (87-418)	4,7 (2,3-7,3)
6th. month					
milk	510	16,5 (11-19)	23,2 (17-31)	46,9 (20-82)	1,7 (0,7-2,3)
flours	50	8,0 (2,5-11,0)	11,0 (1,4-70)	160,0 (44-370)	0,8 (0,6-1,2)
meat	100	4,0 (3-7)	16,0 (10-28)	80,0 (40-130)	2,2 (1,1-3,8)
Total		28,0 (16,5-37)	50,0 (28-129)	287,0 (104-582)	4,7 (2,4-7,3)
7th. 8th. month					
milk	600	19,5 (13-22)	27,3 (21-36)	55,2 (24-96)	2,0 (0,9-2,7)
flours	50	8,0 (2,5-11,0)	11,0 (1,4-70)	160,0 (44-370)	0,8 (0,6-1,2)
meat	100	4,0 (3-7)	16,0 (10-28)	80,0 (40-130)	2,2 (1,1-3,8)
Total		31,5 (17,5-40)	54,0 (32-134)	295,0 (108-596)	5,0 (2,6-7,7)
9th.12th.month					
milk	650	22,0 (14-25)	29,5 (22-39)	59,8 (26-104)	2,1 (0,9-2,9)
flours	70	11,2 (3,5-15,4)	15,4 (2,1-98)	224,0 (63-518)	1,0 (0,8-1,8)
meat	120	4,8 (3,6-8,4)	19,0 (12-33)	96,0 (48-156)	2,6 (1,3-4,5)
Total		38,0 (21-49)	64,0 (36-170)	380,0 (137-778)	5,7 (3,0-9,2)

TABLE IX

Daily intake of Cadmium, Chromium, Copper and Zinc (average diet for adults).

	Cd - mg/d	Cr - mg/d	Cu - mg/d	Zn - mg/d
Soup *	0,013	0,017	0,360	2,066
Main course *	0,008	0,006	0,883	3,900
Dessert *	0,006	0,007	0,099	0,366
Wine (1 litre)	0,008	0,020	0,750	7,300
Water	N.D.	N.D.	N.D.	0,013
Fruit	0,002	0,007	0,102	0,262
Different Foods	0,011	0,017	0,336	2,240
Total	0,048	0,074	2,530	16,147

N.D. = Not Detectable

* = The values for soup, main course and dessert were obtained respectively from pools of various items.

TABLE X

Cadmium, Chromium, Copper and Zinc in some food samples from an African region. (The values are followed by twice the standard deviation).

Samples	Cd p.p.m.	Cr p.p.m.	Cv p.p.m.	Zn p.p.m.
maize flont	< 0,05	< 0,1	1,9 ± 0,1	20,3 ± 1,4
maize paste	< 0,05	< 0,1	1,4 ± 0,2	8,9 ± 0,6
cassava	< 0,05	0,10 ± 0,01	3,3 ± 0,5	13,8 ± 2,5
boilet cassava	0,05	< 0,10	1,6 ± 0,2	5,2 ± 0,4
beans	0,07 ± 0,01	< 0,10	5,6 ± 0,1	25,3 ± 1,5
peanut pastry	0,08 ± 0,02	0,25 ± 0,01	6,1 ± 1,1	28,9 ± 2,1
rice	< 0,05	< 0,10	1,2 ± 0,1	11,1 ± 0,5
rice	< 0,05	< 0,10	2,1 ± 0,2	12,1 ± 1,5
tomates	0,05 ± 0,01	0,20 ± 0,01	8,7 ± 0,7	22,5 ± 2,5
spinach	< 0,05	< 0,10	8,4 ± 0,9	18,2 ± 1,6
vegetable sauce	0,08 ± 0,02	0,10 ± 0,01	3,4 ± 0,1	19,2 ± 1,3

TABLE XI

Ratio Cd/Zn in adults diet:	
Soup	1: 160
Main course	1: 500
Dessert	1: 63
Wine	1: 1000
Fruit	1: 1500
Different foods	1: 200
Total diet	1: 300
Total wine and fruit	1: 200

Ratio Cd/Zn in african food samples:	
Beans	1: 361
Peanut pastry	1: 361
Tomatoes	1: 450
Vegetable sauce	1: 240

Ratio Cd/Zn in babies diet:	
4th. month	1: 121
5th. "	1: 162
6th. "	1: 160
7th.-8th. month	1: 158
9th.-12th. "	1: 150

Ratio Cd/Zn in flour samples:	
1	1: 110
2	1: 63
3	1: 120
4	1: 60
5	1: 115
6	1: 155
7	1: 110
8	1: 112
9	1: 58
10	1: 100
11	1: 250
12	1: 43
13	1: 90
14	1: 100
Average	1: 100

Ratio Cd/Zn in milk and strained foods (average):	
Milk	1: 100
Strained mead	1: 550

Although it is not possible to carry out a complete comparison with similar items produced in Italy the values of cadmium and chromium seem considerably lower in the African samples.

It is known that cadmium is a natural contaminant of zinc and that the ratio Cd/Zn is 1/350 in the earth surface and about 1:100 in foods (average).

Our results (table XI) generally confirm such a ratio, particularly as far as milk and flour are concerned.

These results also suggest that a limitation of cadmium in the diet is impossible unless the zinc is also limited.

In effect considering the ratio of the intake of cadmium and zinc is about 1:300, the latter element should not exceed 30 mg. in the diet.

Higher values could bring into the organism an excess of cadmium.

Acknowledgments

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THE USE OF RADIOISOTOPES ^{32}P AND ^{35}S IN STUDIES ON BEHAVIOUR OF PESTICIDES IN THE SOIL

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ABSTRACT

Activated atoms were used to determine the possibility and extent of contamination of underground waters by pesticides used in agriculture. The sorption and dynamics of the migration of two organo-phosphorous pesticides, fenitrothion and malathion, were studied. These two products are currently being proposed as agricultural pesticides.

They would replace other substances of the chlorinated hydrocarbon group, including DDT, which are more dangerous to health, but are themselves source of potential contamination of underground waters.

Studies were carried out on different types of soil: sandy and clay. Isotherms were determined for the sorption of the pesticides examined, together with their distribution coefficients, Kd. The effects of pH values, exchangeable ions, organic substances (organic C and N) and the mechanical composition of the sorption of fenitrothion and malathion were studied.

1. Introduction

The negative effect of pesticides from the group of chlorinated hydrocarbons on the environment is commonly known. This particularly concerns such persistent pesticides as DDT and lindan as well as aldrin, dieldrin, endrin and heptachlor. In Poland, as in many other countries, the production and use of DDT is gradually being limited with simultaneous introduction of such substitutes as organophosphorus compounds and derivatives of carbamic acid. Our industry is already producing several organophosphorus insecticides as malathion and fenitrothion which may replace DDT in the combat with insects. Organophosphorus pesticides, in comparison with DDT, are much easier subjected to various changes in soil and plants as biodegradation, hydrolysis or oxidation and furthermore can be absorbed by the soil. However, one should consider the possibility of the pesticides being displaced from the soil as a result of rainfall. These factors favour the migration of pesticides and their metabolities to subsoil waters.

This report presents the results of studies on the sorption of fenitrothion and malathion in the soil and the washing out of these pesticides from the soil by rainfall. The investigations were conducted with the use of the radionuclide labelled compound technique, at present often employed in experimental practice.

2. Materials and methods

The investigations were conducted on pseudopodsolic soils taken from top layers /0 - 25 cm/ from which textural groups of soils differing in their mechanical and chemical composition, cation exchange capacity and organic matter, were taken /table I/

The studies were conducted with malathion - ^{35}S with

Table I

Characteristic of soils used for study

Soil - textural groups	Clay <0,002 mm %	Organic matter %	pH		Exchangeable Cations Ca^{2+} + Mg^{2+} in m.e per 100 g
			H_2O	in KCl	
1. Silt loam	4,0	0,77	5,4	4,4	1,6
2. Silt loam	6,0	0,80	5,8	4,9	3,0
3. Silt loam	8,0	0,94	7,4	7,3	7,8
4. Silt loam	7,0	1,54	7,6	7,4	9,8
5. Silt loam	13,0	3,55	6,7	6,4	11,6
6. Sandy loam	5,0	8,47	6,1	5,3	18,7

specific activity 4,5 mCi/mmol and fenitrothion - ^{32}P with specific activity 1,25 mCi/mmol. The labelled pesticides were from the Radiochemical Centre, Amersham, Buckinghamshire, England. 30 cm long glass columns with inner diameter 2.7 cm were filled with 100 g samples of soil dried in the air and then 1 mg of labelled pesticide in 5 ml water solution /malathion - ^{35}S/ or 5 ml diluted ethanol solution /fenitrothion - ^{32}P/ was added drop by drop. The columns of soil were eluted with distilled water imitating rain water. Through each of the columns were passed 350 ml of the distilled water, equalling 616 mm of rainfall. The height of the soil in each of the columns was: 1 - 13,2 cm; 2 - 13,6 cm; 3 - 13,0 cm; 4 - 14,1 cm; 5 - 16,0 cm: 6 - 20,5 cm. After dilution with distilled water the columns of soil were divided into 1 - 2 cm thick layers. The radioactivity of individual portions of the eluate /25 - 50 ml/ and layers of soil was determined. The samples of eluate and soil for radioactivity measurements were prepared in standard aluminum containers with 24 mm inner diameter and 4 mm depth. The activity of fenitrothion - ^{32}P was determined in 0,5 ml of solution and malathion - ^{35}S from 1 ml after evaportion to dryness. The mass of the soil taken for radioactivity measurements was 300 - 500 mg. Additionally a correction was determined for the self-adsorption of activity emitted by the soil. The radioactivity of the samples was determined with Geiger Müller counter type BOH - 42/0 introduced as part of a measuring unit produced by „Polon". Geometry of calculation 2π, and time unit 100s were employed. The activity of samples was calculated for the concentration of the pesticide in μg per soil mass unit or volume of solution.

3. Results of studies and conclusions

The results of the studies on the penetration of fenitrothion - ^{32}P and malathion - ^{35}S through soils with varied mechanical and chemical composition are presented graphically in figures 1 and 2. The axis of ordinates gives the % quantity of pesticides eluted from the soil by distilled water imitating the size of rainfall in mm. Fig 3 presents the adsoption of fenitrothion -^{32}P and malathion - ^{35}S in individual layers of a column on the example of two soils. The studies indicate that fenitrothion - ^{32}P is adsorbed by soils to a much greater degree than malathion - ^{35}S. This is probably due to the difference in the structure of the molecules of the examined pes-

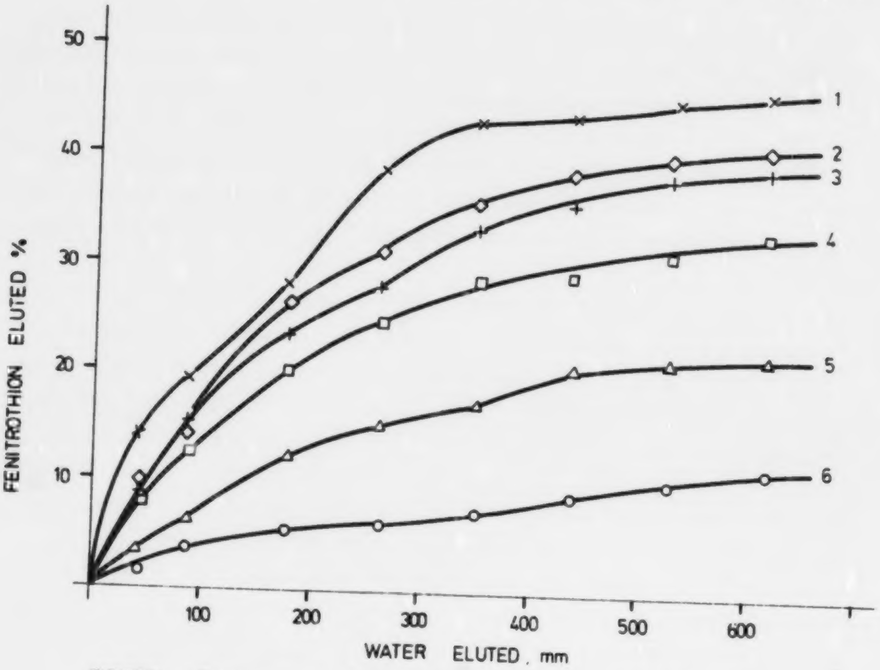

FIGURE 1. ELUTION OF FENITROTHION THROUGH VARIOUS SOILS

ticides. The displacement of pesticides from the soil occurred with rainfall up to about 350 mm and was for fenitrothion - ^{32}P between 10 and 45% and for malathion - ^{35}S between 38 and 76 % of the amount introduced. There has been observed a certain correlation bewteen the content of the clay fraction/<0.002 mm/, ion exchange capacity and content of organic matter in the soil and

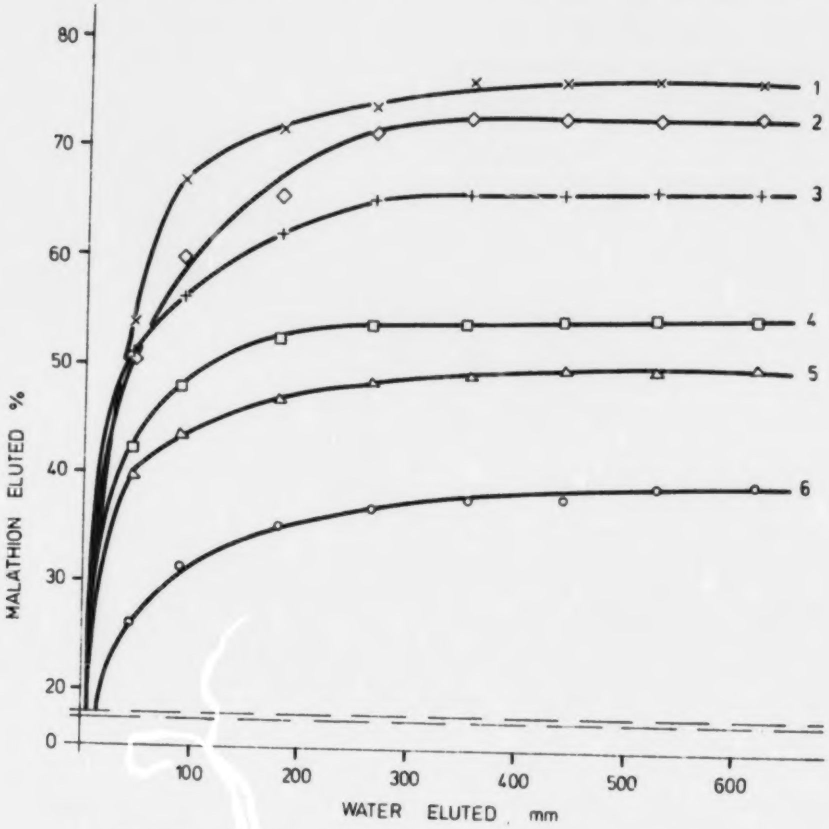

FIGURE 2 ELUTION OF MALATHION THROUGH WARIOUS SOILS

its capacity to absorb malathion and fenitrohion /fig 1 and 2/. The rate of adsorption of the studies solis in µg/g soil is as follows: for malathion - ^{35}S - 1 - 2,3; 2 - 2,7; 3 - 3,4; 4 - 4,6; 5 - 5,0; 6 - 6,1; for fenitrothion - ^{32}P - 1 - 5,4; 2 - 5,9; 3 - 6,1; 4 - 6,7; 5 - 7,8; 6 - 8,9. The sorption of the studied pesticides was not similar for different layers of a column /fig 3/ which may indicate the possibility of the migration of these compounds in soil as a result of rainfall.

The conducted studies allow the following conclusions:
1. Soils have a certain capacity to absorb fenitrothion and malathion and this capacity depends on the mechanical composition, ion exchange capacity and content of organic matter
2. Fenitrothion and malathion can be displaced from the soil due to rainfall which indicates the possibility of their migration to subsoil waters.

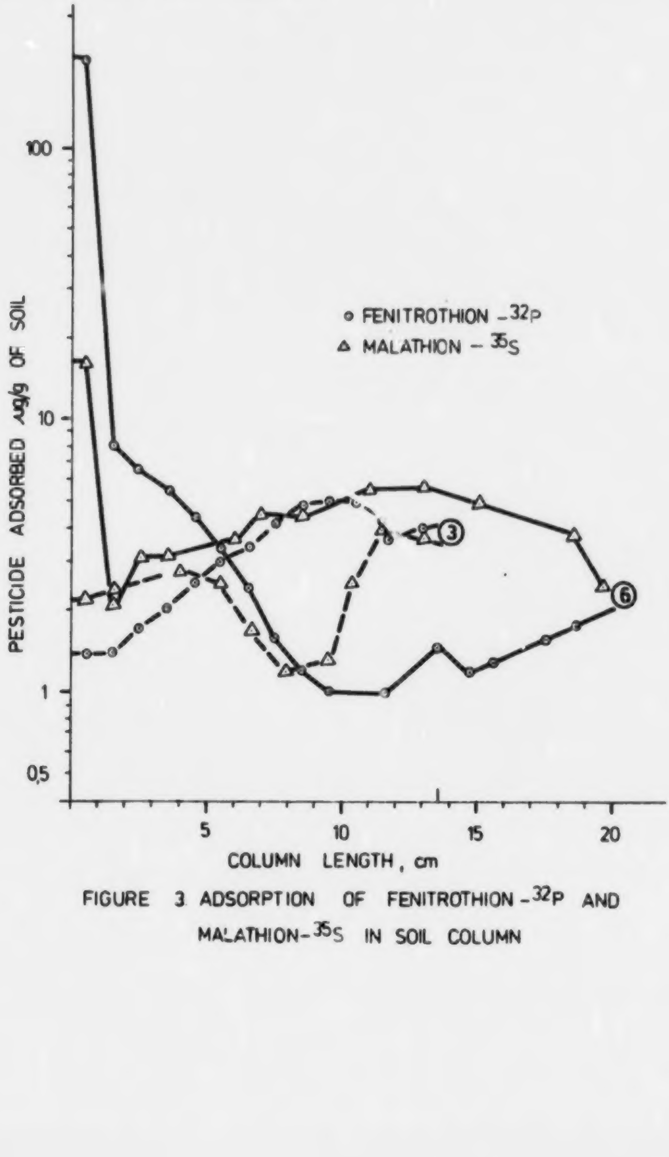

FIGURE 3 ADSORPTION OF FENITROTHION-^{32}P AND MALATHION-^{35}S IN SOIL COLUMN

3. The use of pesticides labelled with radionuclides in investigations on the behaviour of pesticides in the environment facilitates comparatively accurate measurements of low concentrations of these compounds in soil and solutions.

DIE BELASTUNG DER NAHRUNG MIT DEN SCHWERMETALLEN BLEI, CADMIUM, QUECKSILBER, ZINN UND ARSEN IN ÖSTERREICH

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KURZFASSUNG

Aufgrund der statistisch ermittelten Verzehrsgewohnheiten des Österreichers und unter Verwendung der analytischen Daten für Schwermetallspuren in Lebensmitteln wird die Aufnahme von Blei, Cadmium, Quecksilber, Zinn und Arsen abgeschätzt.

Die ermittelten Werte werden für einen Überblick über die durch Lebensmittel aufgenommenen Mengen an potentiell toxischen Schwermetallen in Österreich und für einen Vergleich mit aus der Literatur bekannten Aufnahmedosen in anderen Ländern und internationalen Toleranzen herangezogen.

Darüber hinaus haben wir ausführliche Untersuchungen an verhältnismässig stark mit Schwermetallen kontaminierten Lebensmitteln durchgeführt, wobei sich zeigt, dass es für die Elemente Quecksilber, Cadmium und Arsen jeweils ganz bestimmte Gruppen von Lebensmittel sind, die einen gegenüber den durchschnittlichen Werten anderer Nahrungsmittel erhöhten Gehalt aufweisen. Zinn wird in erheblichen Mengen lediglich in eingedosten Lebensmitteln gefunden, während Blei unregelmässig auf Lebensmittel verteilt ist.

Die ermittelte monatliche Aufnahme an Schwermetallen beträgt pro Person 2,5 mg Blei, 0,6 mg Cadmium, 0,2 mg Quecksilber, 10 mg Arsen und 100 mg Zinn.

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Gemessen an der Schwermetallbelastung in anderen Ländern liegen die in Österreich aufgenommenen Mengen bei Quecksilber, Blei und Arsen verhältnismässig tief, während die nahrungsbedingte Aufnahme von Cadmium an Spitzenwerte industrialisierter Staaten heranreicht. Insgesamt liegen alle Werte weit unter den von FAO/WHO angegebenen vorläufigen annehmbaren Aufnahmedosen.

ABSTRACT

The intake of lead, cadmium, mercury, tin and arsenic is estimated on the basis of statistics on Austrian dietary habits and analytical data on traces of heavy metals in food.

The values obtained are used in a survey of the intake of potentially toxic heavy metals via food in Austria, and in a comparison with intakes (reported in the literature) in other countries, and international tolerance standards.

In addition we carried out detailed investigations of foods which were relatively heavily contaminated with heavy metals. These showed that there are distinct groups of foods which have a high content of the elements mercury, cadmium and arsenic, as compared with the mean levels of these in other foods. Tin is found in considerable quantities only in tinned foods, while lead is irregularly distributed in foods.

The monthly intakes of heavy metals found per person are 2.5 mg lead, 0.6 mg cadmium, 0.2 mg mercury, 10 mg arsenic and 100 mg tin.

Compared with the incidence of heavy metals in other countries, the intakes of mercury, lead and arsenic in Austria are relatively low, while the cadmium intake via food reaches peak levels for industrialized countries. Taken as a whole, all levels are well below the FAO/WHO provisional acceptable intakes.

1.Einleitung

Zur Ermittlung der nahrungsbedingten Schwermetallaufnahme in Österreich wurden die durchschnittlichen Verzehrsgewohnheiten nach Ergebnissen der Konsumerhebung 1964 herangezogen. Wir untersuchten alle Nahrungsmittel, deren monatlicher Verzehr 0,4 kg überstieg, sowie fallweise auch in geringen Mengen konsumierte Lebensmittel. Tabellarisch werden jene Lebensmittel aufgeführt, für die eine besondere Belastung mit einzelnen Schwermetallen festgestellt werden konnte.

2.Belastung der Nahrung mit Schwermetallen

2.1. Blei

Blei zählt wegen seiner hauptsächlichen Verbreitung über Autoabgase zu den systematisch schwer faßbaren Schadstoffen, da der Standort der pflanzlichen Nahrungs- und Futtermittel von Bedeutung ist. Es existieren kaum besonders belastete Lebensmittel. Viele in Autobahnnähe gedeihenden Pflanzen weisen erhebliche Mengen Blei auf [1]. Die Streuung der für bestimmte Lebensmittel erhaltenen Werte ist deshalb auch sehr groß.

Wir fanden, daß hinsichtlich der aufgenommenen Mengen die gewichtsmäßig an der Nahrung stark beteiligten Lebensmittel zur Bleiaufnahme den größten Beitrag leisten. Die Tab. I gibt neben einigen Grundnahrungsmitteln auch einige verhältnismäßig hohe Werte in verschiedenen anderen Lebensmitteln an, die vielfach nur vereinzelt gefunden wurden.

Die abgeschätzte Gesamtaufnahme von 2,5 mg Pb/Person und Monat liegt unter der für hochindustrialisierte Staaten angegebenen Aufnahmedosis von 6-9 mg Pb/Person und Monat.

2.2. Cadmium

Cadmium hat sich als ubiquitär verbreitetes Spurenelement erwiesen. Nach jüngsten Berichten [4] hat in einigen Ländern die Aufnahme von Cadmium mit der Nahrung bereits die Grenze der vorläufigen annehmbaren Dosis der WHO/FAO erreicht. Einzelne Gruppen von Nahrungsmitteln (Tab. II) sind nach unseren Untersuchungen [3] tatsächlich verhältnismäßig stark

Tab. I

Bleigehalte ausgewählter Lebensmittel

Lebensmittel	Proben-zahl	Bereich [ppm]	Gehalt [ppm]
verschiedene Brotsorten	7	0,10-0,61	0,330
Schweinefleisch	7	0,05-0,24	0,157
Fische (konserviert)	18	0,05-0,47	0,190
Milch (frisch)	4	0,08-0,15	0,110
Milch (konserviert)	4	0,20-0,29	0,275
Johannisbeersaft	1	-	0,74
Apfelsaft	2	-	0,72 0,90
Orangensaft	1	-	0,62
Hafer (Ganzkorn)	11	0,90-0,95	0,93
Preiselbeeren-konfitüre	1		0,70

Tab. II

Cadmiumgehalte ausgewählter Lebensmittel [3]

Sorte	Probenzahl	Bereich [ppm]	Mittelwert [ppm]
Mais	3	0,59 - 1,05	-
Weizen	13	0,006- 1,05	0,24
Hafer (Ganzkorn)	4	1,1 - 1,93	1,32
Haferflocken	3	0,007- 0,090	0,045
Haferkleie	1	5,56	-
Gerste	4	0,05 - 0,27	-
Muscheln	39	0,05 - 1,74	0,31
Thunfisch	13	0,05 - 0,97	0,14
Sardinen	27	0,05 - 1,00	0,23
sonstige Fische	65	0,05 - 1,46	0,13
Schweineniere	15	0,01 - 0,41	0,15
Schweinefleisch	15	0,008- 0,025	0,014

mit Cadmium verunreinigt. Dazu zählen die Hüllenmaterialien einzelner Cerealien, Innereien (Niere, Leber) und Muscheln. In einigen Spezialbrotsorten, die sich durch geringen Vermahlungsgrad auszeichnen, fanden wir beachtliche Cadmiumgehalte. Aufgrund unserer experimentellen Daten schätzen wir die Cadmiumaufnahme in Österreich auf 0,6 mg Cd/Person und Monat.

2.3. Quecksilber

Quecksilber findet sich in wenigen Lebensmitteln in beachtenswerter Konzentration. Viele Proben lagen an der Nachweisgrenze der verwendeten Methode [5]. Tab. III enthält eine Aufstellung der mit Quecksilber besonders belasteten Nahrungsmitteln zu denen Thunfische und auch Pilze zählen [6]. Die Gesamtbelastung der Nahrung beläuft sich auf etwa 0,2 mg/Person und Monat und liegt an der unteren Grenze der in der Literatur angegebenen Werte [4, 7].

2.4. Zinn

Hauptquelle der nahrungsbedingten Zinnaufnahme sind in verzinnten Behältern eingedoste Lebensmittel.

Da Zinn unter den betrachteten Elementen die geringste Toxizität aufweist, wird die Zinnaufnahme aus dem Verzehr von Gemüse- und Obstkonserven, Obstsaft- und Fischkonserven allein abgeschätzt (Tab. IV). Basierend auf eigenen Untersuchungen [8,9] ergibt sich aus diesen Quellen eine monatliche Zinnaufnahme von etwa 100 mg. Zu berücksichtigen ist, daß bei einzelnen Gemüse- und Obstsorten eine Anreicherung von Zinn in der Frucht festgestellt wurde, die bevorzugt verzehrt wird [9].

2.5. Arsen

Mit Arsen sind vor allem Muscheln, Innereien und einzelne Räucherprodukte stärker belastet. In einzelnen Fällen weisen auch Biere merkliche Arsengehalte auf (Tab. V).

Die aufgrund unserer Untersuchungen geschätzte Belastung der Nahrung beträgt höchstens 10 mg/Person und Monat und liegt damit deutlich unter Angaben aus der Literatur [10].

Tab. III

Quecksilbergehalte ausgewählter Lebensmittel [5]

Lebensmittel	Probenzahl	Bereich [ppm]	Mittelwert
Thunfische	95	0,005-1,57	0,330
Heringe	71	0,001-0,108	0,025
Sardinen	55	0,001-0,091	0,015
Muscheln	27	0,005-0,077	0,027
Seelachs	10	0,038-0,370	0,101
Reis	7	0,001-0,007	0,003
Teigwaren	3	0,001-0,018	0,007
Eier	6	0,001-0,204	0,056
Pilze (trocken)	7	0,002-2,52	1,376

Tab. IV

Zinngehalt eingedoster Lebensmittel [8,9]

Gemüse- und Obstkonserven	Probenzahl	Bereich [ppm]	Mittelwert [ppm]
Spargel	8	117 - 309	211
Champignon	11	61 - 117	72
Ananas	5	85 - 244	127
Erdbeeren	7	10 - 42,5	25
Bohnen	2	17,5	17,5
Marillen	2	77,5- 97,5	87,5
Pfirsiche	6	19 - 77,5	54
Schwarzwurzel	7	120 - 408	225
Obst- und Gemüsesäfte			
Ananassaft	1	192	192
Gemüsesaft	1	66	66
Grapefruitsaft	4	63 - 95	76
Orangensaft	4	53 - 216	123
Karottensaft	2	15 - 17	16
Tomatensaft	4	16 - 135	32
Zitronensaft	2	25 - 80	52
Fischkonserven			
Muschel	6	20 - 95	44
Sardinen	7	15 - 85	25,5

Tab. V

Arsengehalte in ausgewählten Lebensmitteln

Lebensmittel	Probenzahl	Bereich [ppm]	Mittelwert
Dorschleber	9	0,05 - 3,54	0,88
Muscheln	34	n.n. - 1,20	0,21
Räucheraal	1	0,38	
Tintenfisch	1	0,13	
Bier	4	0,05 - 0,33	0,21
Reis	4	0,02 - 0,09	0,055

3. Diskussion der Ergebnisse

Aus unseren Untersuchungen geht hervor, daß die Schwermetallbelastung der Nahrung in Österreich im allgemeinen unter der stark industrialisierter Staaten liegt (Tab. IV).

Tab. VI

Schwermetallaufnahme aus Lebensmitteln [mg/Person u.Monat]

	FAO/WHO vorläufige annehmbare monatliche Aufnahme	Ermittelter Wert	Literaturangaben	
Pb	12,0	2,5	6-9	[2, 12]
Cd	1,6 - 2,0	0,6	0,45-0,90	[2, 12, 13]
Hg	1,2	0,2	0,2 -0,3	[2,6,11,12]
As	100 (max.Aufnahme)	10	15-70	[10]
Sn	-	100	100	[12]

Die Bleiaufnahme ist deutlich geringer, als beispielsweise in den USA [2].

Der Quecksilbergehalt in Lebensmitteln ist sehr gering, ausgenommen bei bestimmten Fischarten und bei Trockenpilzen. Eine Gefährdung der Gesundheit ist selbst bei starkem Fischverzehr nicht zu erwarten.

Zinn als wenig toxisches Ion gelangt nahezu ausschließlich durch eingedoste Lebensmittel in nennenswerter Menge in die Nahrung.

Die große Empfindlichkeit von Kindern gegen Zinn und Blei muß aber berücksichtigt werden und erfordert laufende Kontrolle.

Arsen findet sich kumuliert in Muscheln und Innereien. Hauptnahrungsmittel weisen dagegen sehr geringe Arsenspuren auf.

Lediglich bei Cadmium konnte festgestellt werden, daß die Belastung der Nahrung im Mittelfeld der Literaturangabe zu liegen kommt.

Wir erachten es deshalb als notwendig, der Überprüfung des Cadmiumgehaltes der Nahrung erhöhtes Augenmerk zu schenken.

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ASBESTOS MEASUREMENTS IN THE CALIFORNIA ENVIRONMENT

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ABSTRACT

The California population is exposed to asbestos from natural sources such as wind and water erosion of asbestos-containing rock formations and from a multitude of anthropogenic sources. Of particular concern are such sources as asbestos mines and mills, automobile brake linings, asbestos spraying for fireproofing of buildings, asbestos cement pipes for transporting drinking water, talcum, and the widespread use of asbestos filters in the food, drug and beverage industries.

Inhalation of asbestos fibers in sufficient quantity is associated with at least three diseases - asbestosis, lung cancer and mesothelioma, with latency periods measured in decades. Thus it is important that long-range monitoring programs be established now to help assess the health effects of this pollutant. The mechanism of pathogenicity may be dependent on the size of the fibers, so monitoring schemes should include size distribution data as well as identification and counting techniques. Since most of the particles of asbestos found in environmental media are too small to be resolved by the optical microscope, electron microscopy must be used. This paper briefly discusses the current status of the sampling methodology and the electron microscopic techniques used to identify, count and size asbestos particles in environmental media and presents data from ambient air sampling near a California asbestos processing plant.

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1. Introduction

This discussion is restricted to the measurement of asbestos in air and water, although much of what will be said is applicable to food, drugs, beverages and other media. The methodology of asbestos quantification in environmental samples falls into four interrelated areas: sampling, preparation of the sample for subsequent analysis, identification, and determination of the concentration of asbestos.

2. Sampling Methods

Air is moved through a membrane filter at a specified flow rate for a length of time determined by the expected concentration of asbestos in the air. For ambient air monitoring, the Air and Industrial Hygiene Laboratory (AIHL) method employs 0.8 μm pore size Nuclepore filters of 47 mm diameter, at a flow rate of ten liters per minute, for 2 to 24 hours.

For water samples, a suitable amount, usually about one liter, is collected in a clean bottle or flask. The water is then passed through a filter, such as Nuclepore, which collects the asbestos particles. Although the filter collection efficiency for small asbestos particles remains to be determined, clearly the smaller the pore size, the higher the collection efficiency. Unfortunately, filtration of water through a small pore filter is a slow process and if, as is usually the case, the water contains many other kinds of particles, the filter may clog before all the water has gone through. It has been estimated that errors of the order of 50% may occur as a result of inefficient filtration through 0.8 micrometer and larger pore size filters.

3. Sample Preparation

Two general classes of sample preparation utilized to obtain size distributions by electron microscopy are the direct-clearing technique and the separation technique. The direct method presents the microscopist with a sample on which a minimum of manipulation has been carried out but which contains both asbestos particles and all other particles which were present in the environmental medium when the sample was collected. The separation technique presents a sample which contains a minimum of interfering particles, but which was prepared with much manipulation.

In many air samples and in some water samples it is possible to use the direct-clearing method to size and count asbestos fibers among the other materials present. In this method the sample filter is coated with a layer of silicon monoxide or carbon to hold the fibers in place. The filter itself is then dissolved by vapors of a solvent such as acetone or chloroform. The film with imbedded fibers and other particles is then examined by electron microscopy. However, urban air containing 100 micrograms of particles per cubic meter will probably contain on the average only 0.01 microgram asbestos per cubic meter. Thus the sample filter contains 10,000 times as much non-asbestos as asbestos material by weight. The ratio of particles depends on the densities and sizes, but for average conditions encountered in urban air will vary from

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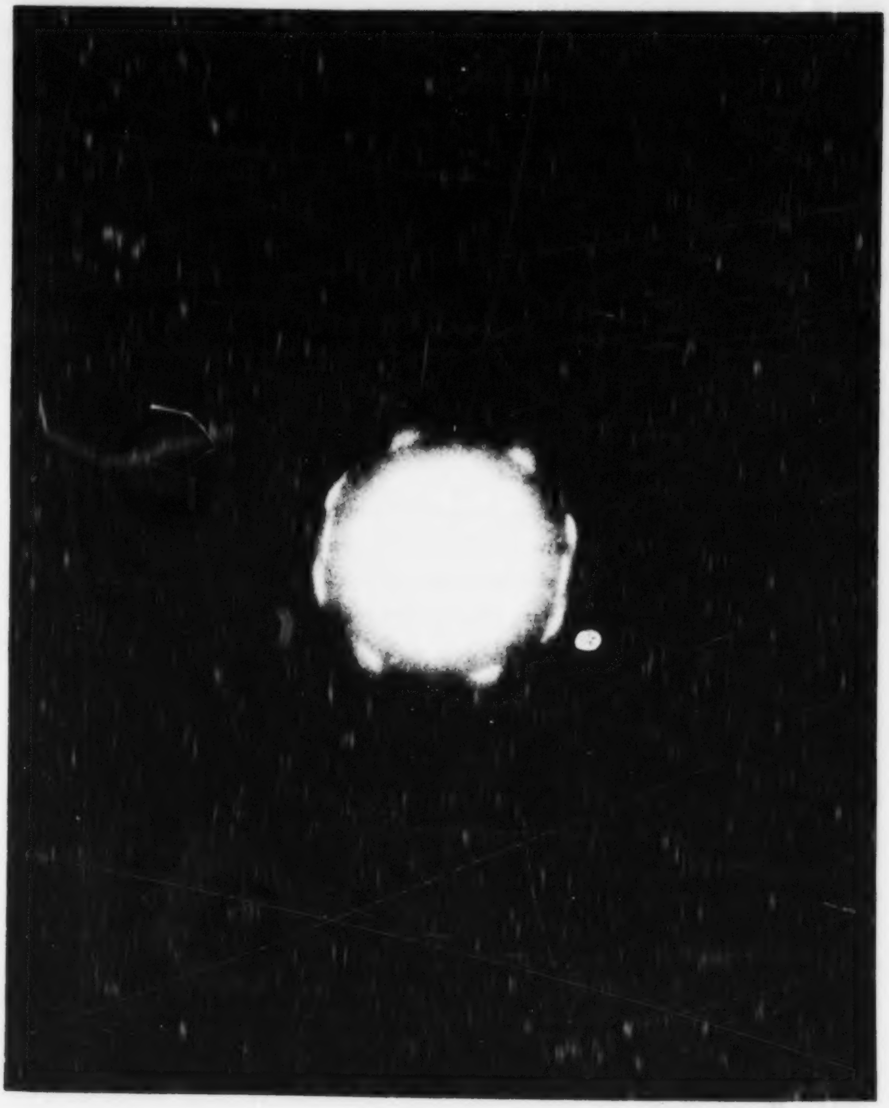


Fig. 1. Diffraction pattern obtained from a chrysotile fiber collected downwind of an asbestos mill.

around 10,000 to 100,000 non-asbestos particles for every asbestos particle. The ratio is even larger in water samples. Under such circumstances, quantitation by the direct clearing technique is difficult.

In the separation technique the filter is ashed to destroy organic particles and fibers, carbon, and the filter material itself. The ashed sample is then mixed with a solution of 0.5% Parlodion in amyl acetate. An aliquot of the suspension is dropped on a water surface within a confined area of known size. Electron microscope grids are then drawn through the asbestos-containing Parlodion film for subsequent counting and sizing, (Smith [1]).

4. Identification and Sizing

After sample preparation, the grid is scanned at 1000X to determine uniformity of sample deposition. The search for fibers is conducted at 8000X. Each fiber detected is identified at 20,000X morphologically and by electron diffraction if necessary. (Seshan [2]). The length and diameter are then measured.

Although chrysotile may be presumptively identified by recognition of a central longitudinal canal in the fibril, positive identification requires electron diffraction. Figure 1 is an example of a diffraction pattern obtained from a chrysotile fiber collected downwind of an asbestos mill. Crystal lattice parameters are computed from such spot and ring patterns and compared with those of standards (Skikne [3]).

This technique allows differentiation of asbestos from non-asbestos materials and of chrysotile from amphibole asbestos. It does not, however, normally allow the identification of the specific type of amphibole present. Fibrils smaller than 0.05 μm in diameter seldom produce diffraction patterns suitable for identification.

Since electron diffraction identification is slow and expensive, in most cases, only 5% of the morphologically-identified asbestos fibers have their identifications confirmed by electron diffraction.

After examining a minimum of 20 grid holes per each of three grids for each sample, the total number of fibers in each size category is calculated, producing the size distribution.

5. Asbestos Size Distribution Data

An experiment was conducted to determine the feasibility of measuring the concentration and size distribution of asbestos fibers in ambient air near an asbestos processing plant using the Parlodion method developed by AIHL. Sampling was carried out at a chrysotile asbestos mill located near King City, California. The asbestos ore and spent ore were stored in unprotected heaps upon the ground within the plant's perimeter. This storage, combined with strong summer winds, made the operation a possible source of airborne asbestos.

One sampler was located approximately 500 meters northwest of the source and another 100 meters southwest. Samples were collected for three hours during the afternoon of

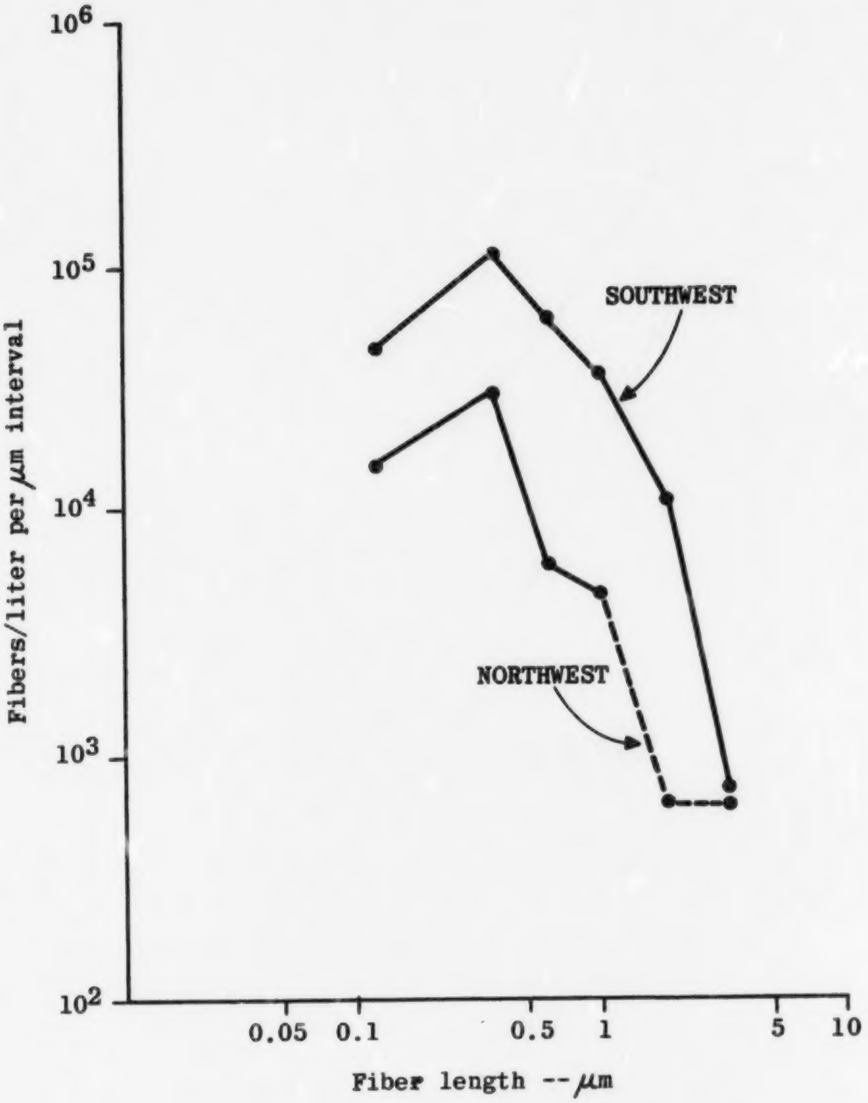


Figure 2 -- Asbestos fibers in ambient air near asbestos mill shown by fiber length. Points connected by dashed lines represent the limit of detection in those size intervals where no fibers were observed.

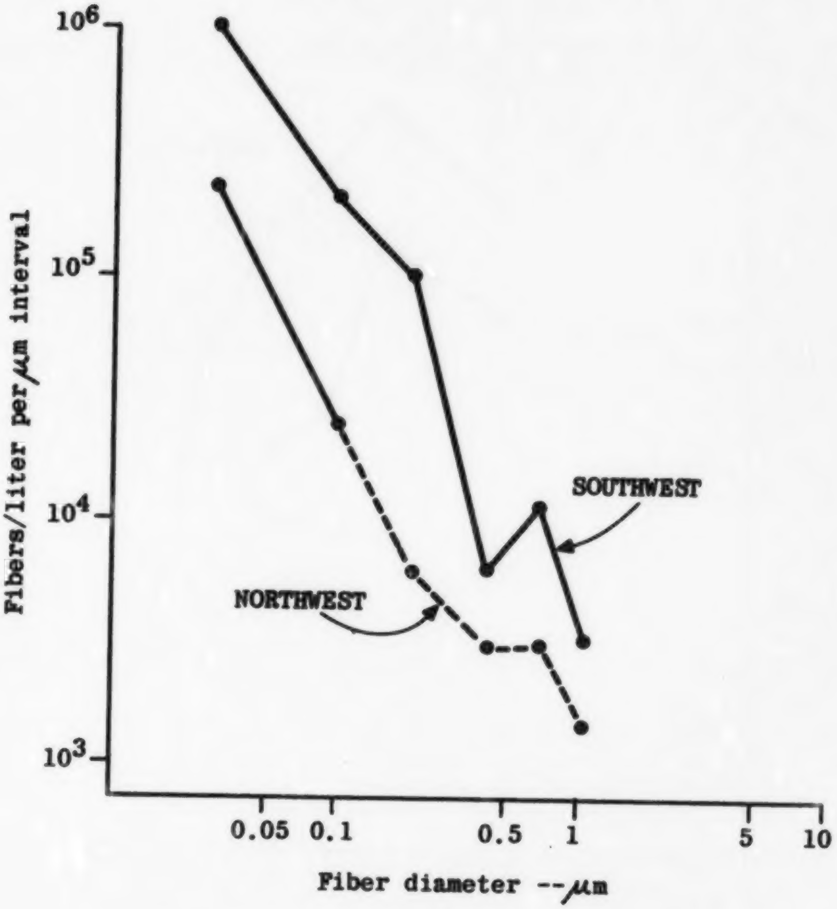
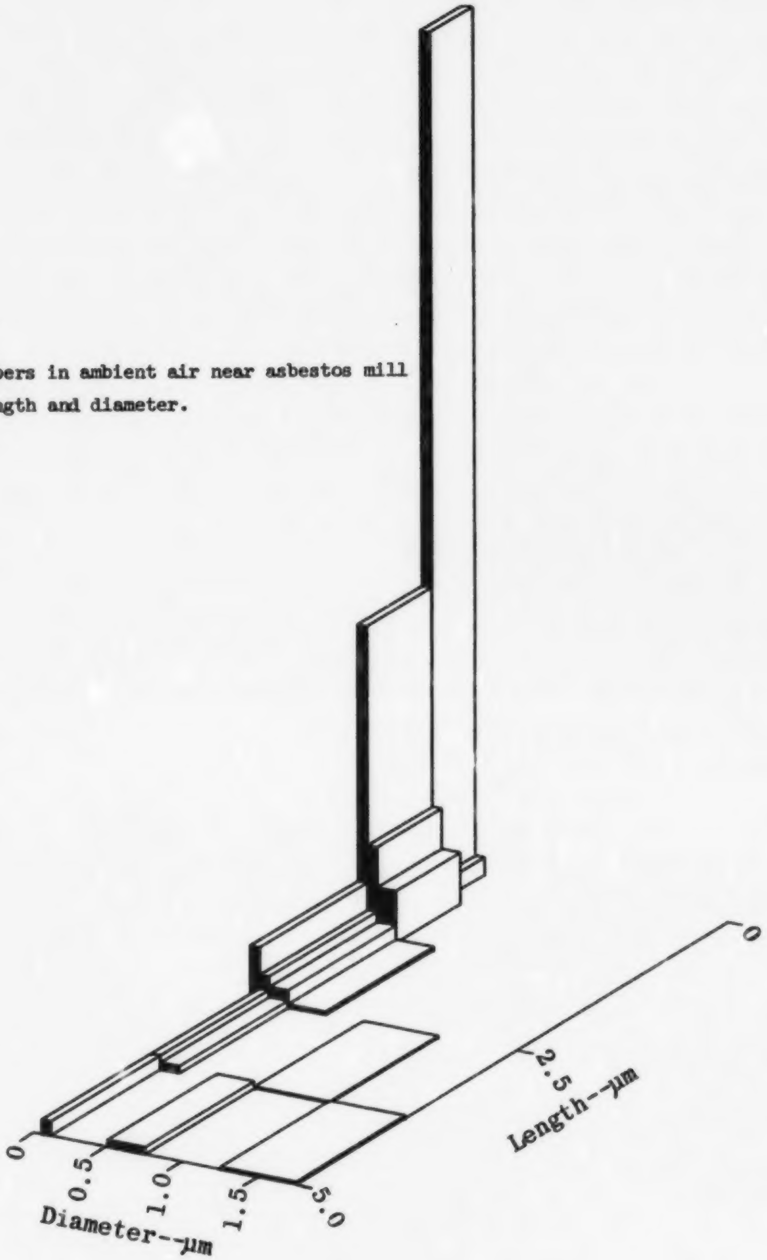


Figure 3 -- Asbestos fibers in ambient air near asbestos mill shown by fiber diameter. Points connected by dashed lines represent the limit of detection in those size intervals where no fibers were observed.

Figure 4 --

Asbestos fibers in ambient air near asbestos mill shown by length and diameter.



April 26, 1972. During this sampling period the weather was clear, the temperature averaged 65°F and the wind blew steadily from the northwest at an average velocity of 600 cm/sec, occasionally gusting to 1300 cm/sec. Due to the location of the mill at the base of a 100 meter hill, the wind trajectory may be complicated. Thus both samplers would be expected to collect source emissions, with the northwest or "upwind" sampler collecting less. Figures 2 and 3 give the fiber size distributions for length and diameter. As expected the "downwind" sample has a greater number of fibers than the "upwind", and the mean fiber diameter is slightly larger. Figure 4 is a three-dimensional plot of the number of asbestos fibers by length and diameter "downwind" of the plant. The number of fibers per liter is shown by the height of the column plotted over the appropriate cell in the length by diameter matrix. The plot demonstrates that the large majority of the fibers are both thin and short (less than 0.5 μm in diameter by less than 2.5 μm long). The "upwind" plot is similar but with slightly smaller fiber diameter.

AIHL has also carried out similar asbestos characterizations for other ambient air locations in California and for water samples collected from rivers and taps. Although there are variations in the shapes of the distributions and in the concentration of fibers present, all samples demonstrate that the large majority of the fibers are too small to be detected by light microscopy.

6. Conclusions

We have demonstrated the applicability of electron microscopy using the Parlodion method for characterizing the fiber size distribution of asbestos. Further, our data, as well as that of others, clearly show that most fibers are too small to be detected by light microscopy, thus making electron microscopy a necessary tool for assessing the health impact of environmental asbestos.

Acknowledgements

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EXPOSITIONSMESSUNGEN

EXPOSURE MONITORING

MESURE DE L'EXPOSITION

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SITING CONSIDERATIONS FOR AIR QUALITY MONITORS AS APPLIED TO EPIDEMIOLOGICAL STUDIES

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ABSTRACT

Every honest researcher has the insecurity that his conclusions may be biased by measurement technique or the environments in which the tests were conducted. A difficulty we have always had is "have we measured what we think we have measured?"

There are three factors in any of the environmental investigations. Those factors entail the inner-relationships between the emission, the transport and the effect on the object or organism in question. Thus, in any assessment of effect of any environmental assault, one must consider the characteristics of the emission and the effect of its transport media before arriving at the receptor. This is especially true in "ambient" monitoring.

Epidemiological studies using air monitoring data, including those data provided by persons whose monitoring purposes are other than epidemiological, usually are accepted on face value. It can be shown that the ambient air quality is very sensitive to the placement of the sensor, relative to the emission source. Thus, correlations of this data with respect to health effects can become overly biased, according to this placement. Some currently important pollutants are discussed with respect to these siting considerations and the relationship between sources and the ultimate receptor exposure.

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This paper presents some suggestions for siting of air quality monitors with respect to the pollutant and its source. It is imperative that perspective air quality data be investigated to assure that the data is not overly sensitive to the sensor location.

1. INTRODUCTION

It is well known that much of the available air quality data, historically as well as presently generated, contains many points where the data becomes sensitive to interference parameters that are undesirable and unknown to the final user. The three major influences on data as gathered for air quality measurement purposes are:

1. Unknown variation in emissions
2. Sensitivity to various types of transport conditions(meteorology)
3. Sensitivity of the instrument site to local phenomenon

Unless the above influences are properly described in the statistics, the conclusions can easily be misleading.

Most standard techniques use a large sample taken at various physical locations in order to come to their conclusions. Correlations with various population groups are taken as subsequent analysis. Usually, those data points lying outside "acceptable" to the models are discarded. There is always the danger that these exceptions may be the rule. In lieu of meaningful documentation one can easily rationalize that this is the best alternative.

It is this researcher's opinion that it is better to work at the "front end" of the problem: either document the existing station so as to show its relationship to its immediate environs, or survey a potential site in order to place the sensor at a point which will optimize the sensitivity to the function which one is trying to describe.

2. EMISSION CONSIDERATIONS

When using air quality data one must be fully aware of the variations of the emission rates in both the immediate and general area surrounding the sensor. A case in point is sulfur dioxide. Since sulfur containing fossil fuels are used extensively in heating of space (space heating), as well as industrial and power generation uses, there is a base line on which a seasonal variation is super-imposed. This phenomenon is usually accentuated by the use of "cleaner" fuels in a scheduling called "interruptible service". In the northern United States clean fuels are used in the warmer months. In colder months the residential heating units use the cleaner fuel, but the industrial and electrical industries use fuels containing more sulfur.

Suspended particulate also has seasonal variation. In Chicago typical maximum months would be May and June as well as the winter months. The minimum is typically in July, caused by the variation of the agricultural activities, July being the maximum growing month and minimum tillage. This emission variation, both from natural and man-made sources, linked with the greater frequency of inversions during the latter part of the summer, lead to an interesting variation.

3. TRANSPORT AND METEOROLOGY

The variations in temperature, rainfall, wind speed and wind direction play a great part in the measured concentrations of any of the pollutants. As for suspended particulate, temperature as well as the rainfall and growing season make a large difference in the total measured during various months of the year. In most areas winter winds are stronger and more northerly, whereas the summer wind speeds are much less. Frequencies of stagnation and/or inversions are greater. All air quality values are dependent upon these parameters. If one considers re-suspension as a significant source of particulate [1] there is a point at which increased wind speeds increase the particulate which is contradictory to most modeling considerations.

Parameters such as ozone are almost completely dependent upon solar radiation but are also dependent upon natural sources. It is well known that many photo reactive organic materials are emitted by natural processes of plant respiration and metabolism. Similar statements can be made concerning hydrocarbons. Location of meteorological monitoring equipment is extremely important. Many times it is overlooked to the point where not only technical skills have been neglected but common sense also has been ignored. Thus transport and meteorology are important controlling factors as to the concentrations of air quality sensed at any single point.

4. SITING OF SENSORS

The technique of properly siting air quality instruments is not at all well developed. Each situation exhibits a unique local environment. Location and deployment of air quality sensors are thus left to the individual under broad guidelines. The final user of the information is at a disadvantage. He usually has to accept the information without question and without full confidence that the air quality data presented is representative of the organism's exposure.

Two examples are presented in Figure 1 and Table 1. Figure 1 represents a location where the sensor is located six feet above the lip of a depressed expressway. Portable carbon monoxide sensors were deployed on 27 occasions under various meteorological conditions. The nearest residence was approximately 50 feet from the telemetry station. The hypothesis was that the telemetry station is not representative of human exposures. As one can see from the results, the nearest household was exposed to approximately one-half of the concentrations seen at the telemetry station. Correlation with health effects with this historical station would, indeed, be spurious unless this factor was taken into consideration.

Table 1 represents a three-day study at three different stations throughout the city of Chicago so as to determine the height dependence relative to total suspended particulate. It is easily seen that the lower sensors recorded higher values. This fact, combined with the information that most of this added particulate was in a larger "non-respirable" size range, makes the correlation between suspended particulate and health indeed difficult. Similarly, Table 2 shows the height dependence of the highest and lowest station in the Chicago air quality network. These stations are located within two city blocks of each other. Both sensors are above the city-wide average for total suspended particulate and are located in the business and commercial center of

TABLE 1

High/Low 24-Hour Concentration of Suspended Particulate at Selected Stations

Station	Geographical Description	Sensor Height Above Ground Level (in feet)		Concentration (in ug/m^3)		
		High	Low	High	Low	Difference
1. Clay	Industrial	57	19	32	81	49
				--	75	
				113	98	-15
2. Stevenson	"Clean" Residential	51	-6	56	67	11
			(Hi-Vol located in a depression)	94	70	-24
				84	91	7
3. Austin	"Dirty" Residential	61	10	100	152	52
				82	127	45
				52	91	39

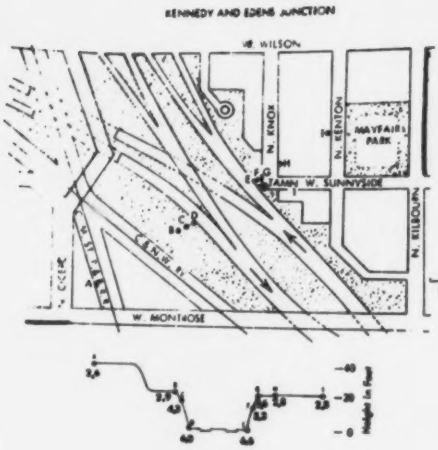

Fig. 1. Composite of 27 sets of samples for carbon monoxide across a juncture of two expressways. A telemetry station is designated as TAMN 1. The nearest occupied residence is at "H". Note that the nearest residence is exposed to 25% less than at the telemetry station and less than half that of the expressway.

TABLE 2

Loop Area Study of Height Dependence of Suspended Particulate Concentrations (24-Hour Hi-Vols)

1. CAMP Station:
   12' Height - Severe Canyon Exposure

2. GSA Building:
   133' Height - Moderate Canyon Effect

Date		Concentrations (in ug/m^3)		
		CAMP	GSA	Difference
	Oct. 12/72	218	72	+ 146
	15/72	109	61	48
(Sun.)	17/72	179	78	101
	19/72	239	150	89
	29/72	94	41	53
(Sun.)	31/72	121	74	47
	Nov. 2/72	127	87	40
	5/72	143	124	14
(Sun.)	7/72	146	93	53
	9/72	299	128	171
(Sun.)	14/72	163	68	95
	16/72	199	171	18
	19/72	94	65	29
(Sun.)	21/72	218	113	105
	23/72	140	63	77
	26/72	63	-	-
(Sun.)	28/72	210	105	105
	30/72	262	145	117
	Dec. 3/72	170	33	137

metropolitan Chicago.

It is well known that ozone is quickly converted by NO to oxygen. Thus, in the areas of large automobile traffic where some NO is emitted directly from the exhaust pipe, ozone concentrations are relatively small. Maximum ozone concentrations will occur two to three hours downwind of the source regions and at higher levels. At this point the ozone would be well mixed.

Hydrocarbons, like suspended particulate, are a catch-all category for many compounds and combinations. Since many hydrocarbons are emitted, both by stationary as well as mobile sources (automobiles), it is difficult to correlate this parameter with those health effects under presently available data.

Finally, sulfur dioxide usually will decrease as the sensor height is decreased. Most sensors are located on building roofs slightly below the horizontal centerline of the plume. The further one departs from the centerline the less the concentrations become. (The opposite condition is true with total suspended particulate due to reflotation phenomenon.)

5. CONCLUSIONS

The above comments are a brief description of some of the variables not always considered in the statistics and monitoring of air quality data. We will probably never rid ourselves of these difficulties. However, some suggestions can be made. The most important is that one should gain a full knowledge of the local environs, both through visitation and photographs and obtain first hand evidence of possible local influences. Portable sensor documentation such as presented in Figure 1 is invaluable. Prevention is always the better quality. Thus when deploying sensors for such studies one should document the area in question, placing the sensors so as to best represent the people exposure. Finally, any conclusion of the health effects and standards for air quality data should include some description of the sensors, location and exposure with respect to the organisms. A case in point is the current guideline for siting of carbon monoxide sensors where the sensor can vary from the curb up to twenty feet from the curb, 15 feet high! Thus, unless the researcher knows fully the variation in concentrations between these two extremes as related to the people in that area, the best standards become absurdities relative to the variation in concentration possible through inadequate siting criteria and guidelines.

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EVALUATION OF A RAPID INDEX OF ENVIRONMENTAL POLLUTION BY TOBACCO SMOKE AND STUDY OF THE COMPOSITION OF THE MAIN-STREAM AND SIDE-STREAM CIGARETTE SMOKE

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ABSTRACT

The Authors refer the results of the researches direct to study the composition of both the main-stream and side-stream cigarette smoke.

The constituents detected are: tar, nicotine, CO, CO_2, NO_2, NH_4^+, *and some polycyclic aromatic hydrocarbons: Pyrene, Anthracene, 3,4-Benzpyrene.*

From the results the Authors point out that the quantities of tar and nicotine found in the side-stream are greater than those present in the main-stream smoke, with the only exception for the nicotine in the B) without filter cigarettes. In all other cases the ratio between the side-stream and main-stream smoke is: about 2 for the tar in no-filter cigarettes and from about 2 to about 6 for filter cigarettes; for the nicotine about 2 for no-filter and from about 2 to about 4.5 for filter cigarettes.

With regard to the gas-phase, the different gases are differently distributed in the two portions, but, with the exception of CO, they are also found in greater measure in the side-stream than in the main-stream smoke.

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The Authors note that the polycyclic aromatic hydrocarbons are also formed during the period of non-inhalation and that the quantity of 3,4-Benzpyrene found in the side-stream corresponds to more than 2,5 times that present in the main-stream smoke.

An index useful for a rapid evaluation of environmental pollution by cigarette smoke has been worked out and CO was chosen as a significant index, because: it is always present in very high quantities in room-air where people smoke; in these ambients, if they are rationally heated, it is only produced by tobacco smoke; it may be evaluated easily, rapidly and exactly by "Draeger System".

From CO, using formulas proposed by the Authors, it can work out other indexes, as the 3,4-Benzpyrene, and calculate also the equivalent number of cigarettes a non-smoker would in theory have passively smoked breathing for a some time the smoky air of social meeting rooms.

1. Introduction

The current literature concerning the toxic and carcinogenic substances present in the inhaled portion of cigarette smoke is very rich and exhaustive; on the contrary the researches directed to study the composition of the cigarette smoke dispersed in room-air, in order to evaluate the environmental pollution by tobacco smoke and to assess the danger to which no-smokers are exposed in rooms where other people are smoking, are few and fragmentary.

The papers by Wynder [1], Kotin and Falk [2], Galuskinova [3], Neurath et al. [4], Ferri and Baratta [5], on the distribution of some compounds in the different portions of cigarette smoke, should however be mentioned.

2. Experimental

For this purpose, we have carried out different researches, already published (Scassellati Sforzolini and Saldi [6], Pascasio et al. [7], Scassellati Sforzolini et al. [8], Savino and Scassellati Sforzolini [9], Scassellati Sforzolini and Savino [10]), that we summarize here.

In these studies we used apparatus able to smoke cigarettes reproducing human smoking (according to the standard parameters) and to collect separately and contemporarily both the main-stream and side-stream cigarette smoke (Fig . 1 and 2).

2.1 Detection of tar, nicotine and some gases in the main-stream and side-stream cigarette smoke.

The determinations were carried out on different kinds of cigarettes, with and without filter, and the results shown on Table I.

From the results it is seen that the amounts of tar and nicotine found in the ambiental smoke are greater than those present in the smoke inhaled by the smoker; the only exception is for the nicotine of B) no-filter cigarettes. In all other cases the ratio between side-stream and main-stream smoke is: about 2 for the tar in no-filter cigarettes and from about 2 to about 6 for filter cigarettes; for the nicotine equally about 2 for no-filter and from about 2 to about 4.5 for filter cigarettes. With regard to the gas-phase, the different gases are differently distributed in the two portions, but, with the exception of CO, these also are found in greater quantities in the ambiental portion of smoke.

2.2 Detection of some polycyclic aromatic hydrocarbons (P.A.H.) in the main-stream and side-stream cigarette smoke.

The determinations were made on a single kind of cigarette without filter.

On Table II the distribution of some P.A.H., taken as indexes, in the two portions of smoke is represented.

From the values shown on the table, it can be seen that these

Table I

Distribution of tar, nicotine and some gases in the main-stream and side-stream cigarette smoke (mg/cigarette).

Kind of cigarette	Portion of smoke	Tar	Nicotine	CO	CO_2	$NO + NO_2$ detected as NO_2	NH_4^+
A) No-filter	Main-stream	17.7250	0.7915	23.1100	55.4200	0.0130	0.1375
	Side-stream	38.4900	2.0660	4.9425	56.9884	0.0550	8.0000
A) Filter	Main-stream	8.3650	0.4564	22.2200	72.5300	0.0120	0.1000
	Side-stream	33.6800	1.7550	2.9673	98.4344	0.0770	7.5000
B) No-filter	Main-stream	18.8193	0.9531	23.4100	56.0100	0.0150	0.1875
	Side-stream	38.8447	0.8695	3.2950	93.2537	0.0550	7.5000
B) Filter	Main-stream	11.9580	0.4608	21.8000	72.5000	0.0120	0.1500
	Side-stream	35.3297	0.7992	4.9425	56.9884	0.0770	7.0000
C) No-filter	Main-stream	26.0481	1.0337	18.9000	79.2100	0.0160	0.1687
	Side-stream	54.9800	2.1273	3.2950	88.0729	0.0440	6.6500
D) Double-filter	Main-stream	4.3253	0.1451	12.0000	49.5000	0.0080	0.0500
	Side-stream	27.1000	0.6524	2.6360	93.2537	0.0770	5.5000

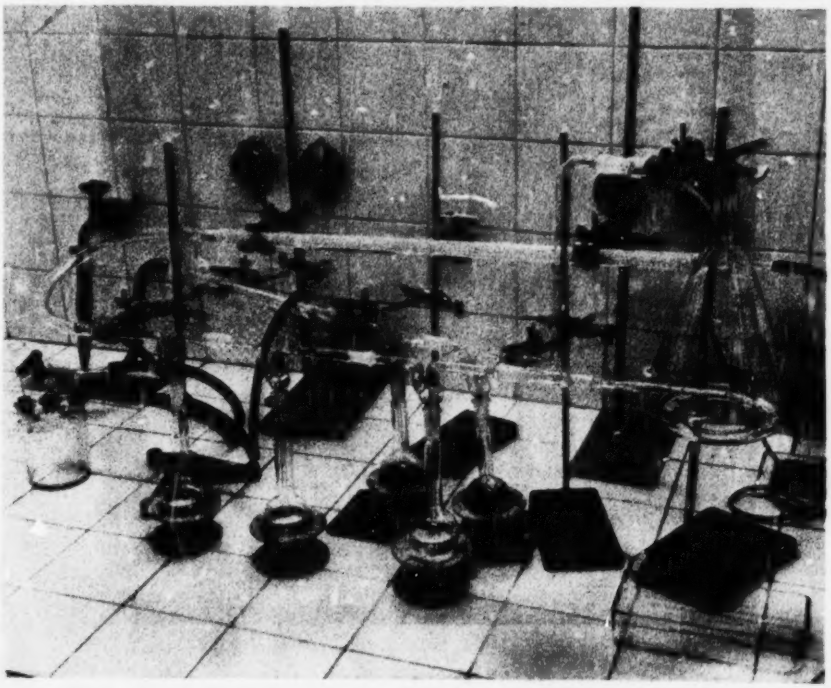

Fig. 1. Apparatus able to smoke and to collect separately both the main-stream and side-stream cigarette smoke: detection of tar and nicotine.

Table II

Distribution of some P.A.H. in the main-stream and side-st eam of cigarette smoke.

P.A.H.	µg /100 cigarettes	
	main-stream	side-stream
Anthracene	4.75	5.40
Pyrene	4.56	1.77
3,4-Benzpyrene	2.54	6.51

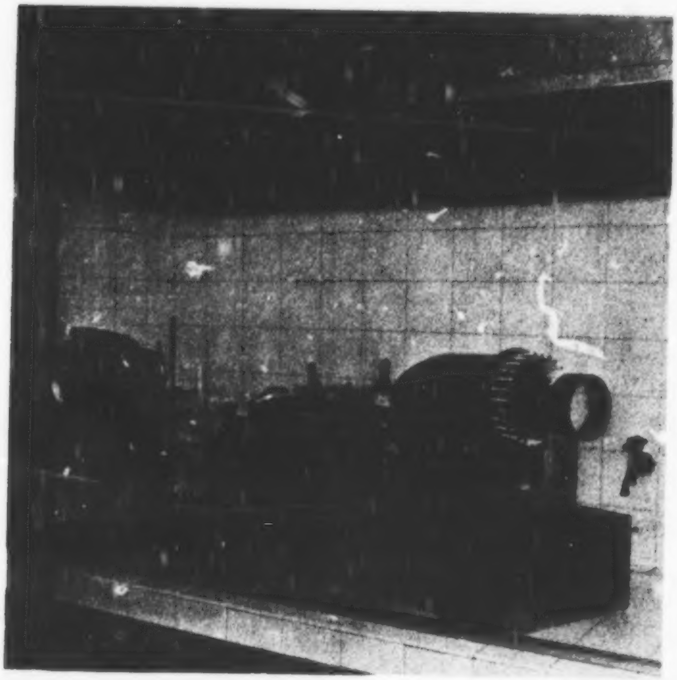

Fig. 2. Apparatus able to smoke and to collect separately both the main-stream and side-stream cigarette smoke: detection of gases and P.A.H.

hydrocarbons are formed during the period of non-inhalation and that, with regard to 3,4-Benzpyrene, the amount found in the side-stream is more than 2,5 times that present in the main-stream smoke of the same king of cigarettes.

2.3. Evaluation of a rapid and significant index of enrivonmental pollution by cigarette smoke.

From what is reported in 2.1 and in 2.2, it can be deduced that the carbon monoxide may be taken as a significant index for a rapid evaluation of environmental pollution by tobacco smoke, because: it is always present in very high quantities in room-air where people smoke; in these ambients, if they are rationally heated, it is only produced by tobacco smoke; it may be evaluated easily, rapidly and exactly by the "Draeger System".

From the ppm of CO measured in the room-air, it can calculate other pollutants present, as the 3,4-Benzpyrene (3,4-BP). In fact transforming the ppm of CO to mg/m^3, making the ratio between the quantities of 3,4-BP and those of CO present in the side-stream smoke (see tables) and considering that the rate of air inhaled by a man under normal conditions is about 500 l/h (Bell et al. [11]), it can calculate the amount of 3,4-BP taken in 1 hour and also the equivalent number of cigarettes a non-smoker would in theory have passively smoked breathing for 1 hour the smoky air of that place, using the following formulas:

$$\underline{\mu g \text{ of } 3,4\text{-BP inhaled}/h} = \text{ppm CO} \cdot \underline{A} \cdot \underline{B} \cdot \underline{C} \qquad (1)$$

where: $$\underline{A} = \frac{CO \,.\, t_0}{t \,.\, V_0} = \frac{28\,010 \,.\, 273}{(273+20) \,.\, 22\,414} = \underline{1.1644}$$

$$\underline{B} = \frac{X}{Y} = \frac{0.0651}{3.68} = \underline{0.0177}$$

X = µg of 3,4-BP in the side-stream smoke of 1 cigarette
Y = mg of CO " " " " "

$\underline{C}$ = air inhaled under normal conditions = $\underline{0.500\ m^3/h}$

$$\underline{\text{equivalent n° of cigarettes passively smoked by a non-smoker}} = \text{ppm CO} \,.\, \frac{\underline{A} \,.\, \underline{B} \,.\, \underline{C}}{\underline{D}} \qquad (2)$$

where: $\underline{D}$ = µg of 3,4-BP in main-stream smoke of 1 cigarette

e.g.: if in the room-air there are 10 ppm of CO (an amount very frequently found in places where people smoke), we have:

$$\underline{\mu g \text{ of } 3,4\text{-BP inhaled}/h} = 10 \cdot 1.1644 \cdot 0.0177 \cdot 0.5 = \underline{0.1030}$$

$$\underline{\text{equivalent n° of cigarettes passively smoked by a non-smoker}} = 10 \,.\, \frac{0.0103}{0.0354} = \underline{4.05}$$

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BEEINFLUSSUNG DES KOHLENMONOXIDSPIEGELS DURCH LÜFTUNGSTECHNISCHE ANLAGEN

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KURZFASSUNG

Es ist bekannt, dass in lüftungstechnischen Anlagen partikuläre Substanzen durch Filter abgeschieden werden können. Hinsichtlich der gasförmigen Substanzen ist dies bislang ungeklärt, wenn man von grosstechnischen Anlagen (z.B. SO_2*-Abscheidung in Rauchgaswäschern) absieht. So wurden für Kohlenmonoxid, das in Hauptverkehrsstrassen den gesundheitsgefährdenden Bereich oft erreicht, indoor-outdoor-Messungen vorgenommen.*

Die CO-Bestimmungen wurden vor und hinter lüftungstechnischen Anlagen durchgeführt, von denen die erste nur aus einem Gebläse ohne Filterung (Abluftanlage einer Tiefgarage) und die zweite aus Faser-Filtern, Aktivkohlefilter, Dampfbefeuchtung und weiteren notwendigen Aggregaten (Klimaanlage in einem Bürogebäude) bestand.

Die Messungen haben gezeigt, dass Kohlenmonoxid in den Anlagen nicht abgeschieden wird, so dass in Übereinstimmung mit anderen Autoren die Aussenluftkonzentrationen in gleicher Höhe auch im Innenraum erwartet werden müssen.

Wenn daher bei vorgegebener hoher Immissionsbelastung eine Klimaanlage installiert wird, muss sie so gestaltet werden, dass der Ansaugstutzen für die Aussenluft in grössere Höhen oder in andere bodennahe Bereiche gelegt wird, die weniger Kohlenmonoxid enthalten.

ABSTRACT

It is well known that particles can be filtered out by air conditioning plants, but with regard to gases the situation is still uncertain, except in the case of large plants (for example the extraction of SO_2 *by flue-gas scrubbers). Accordingly, indoor and outdoor measurements were made of carbon monoxide, which on main roads often reaches levels dangerous to health. Measurements were carried out at the intake and exhaust sides of two ventilating plants, one of which (the extraction ventilator of an underground garage) was simply a fan without a filter, while the other (the air-conditioning plant of an office building) comprised fibre filters, an activated charcoal filter, steam humidification, and other necessary units.*

The measurements showed that carbon monoxide was not removed by air-conditioning plants, so that the concentration indoors must be expected to be as high as the concentration outdoors. This is in line with the views of other authors.

Hence, if an air-conditioning plant is installed where there is a high exhaust gas level, the external air intake must be located at a high point or, if at a low level, at a point where the carbon monoxide content is lower.

1. Einleitung

In den letzten Jahren wurden zahlreiche Gebäude erstellt, deren Innenräume oft teil- oder vollklimatisiert sind. Die Notwendigkeit einer Klimatisierung wurde nicht nur unter dem Gesichtspunkt einer ausreichenden Ventilation gesehen, die bei Großräumen durch Öffnen der Fenster nicht erreicht werden kann, sondern sie wird auch gefordert in der Annahme, daß die Luft in klimatisierten Räumen eine bessere Qualität aufweise als die Außenluft. Hinsichtlich der Abscheidung von Feststoffen durch Faserfilter verschiedener Güteklassen trifft diese Prämisse zu. Ob sich gasförmige Substanzen auch in den Aggregaten lüftungstechnischer Anlagen abscheiden, ist bislang nicht ausreichend geklärt (1,4,5,6), so auch nicht für den Hauptbestandteil der Kfz.-bedingten Luftverunreinigungen, das Kohlenmonoxid, das den MIK-Wert in verkehrsbelasteten Regionen erreicht (2,3). Da klimatisierte Gebäude häufig an Hauptverkehrsstraßen mit hoher Immissionsbelastung liegen, ist es daher von großem Interesse, den Gehalt der Luft an Kohlenmonoxid vor und nach ihrer Passage durch eine Klimaanlage zu untersuchen. Zu diesem Zwecke wurden Untersuchungen an zwei Anlagen durchgeführt, wobei nur ein Ausschnitt aus den durchgeführten Messungen dargestellt werden kann.

2. Versuchsmethodik

2.1. Tiefgarage

In einer Tiefgarage mit drei Stockwerken, die von Kraftfahrzeugen unterschiedlich frequentiert wurden, wurde die Abluft durch ein etwa 30 m langes, aus Mauerwerk bestehendes Kanalnetz über Dach eines nahegelegenen Hauses abgeführt. Die mechanische Entlüftungsanlage bestand nur aus einem Gebläse ohne zusätzlicher Filterung.

Die Meßpunkte waren alternierend in drei Etagen der Tiefgarage sowie im Bereich hinter dem Abluftkanal auf dem Dach in der freien Atmosphäre angeordnet.

Die CO-Messungen erfolgten mit Dräger-Röhrchen Kohlenmonoxid 5/c, deren relative Standardabweichung 15 - 10% beträgt. Entsprechend der Gebrauchsanweisung wurden 10 Hübe gemacht, Die gleichzeitig erhobenen Meßwerte aus den drei Decks der Tiefgarage wurden zu einem arithmetischen Mittelwert zusammengefaßt und den Werten im Abluftschacht gegenübergestellt.

2.2. Klimatisiertes Gebäude

Die Außenluft wurde 6 m über Niveau einer Hauptverkehrsstraße entnommen und in einem Kanal aus Zinkblech etwa 10 m abwärts in ein Installationsgeschoß geleitet, wo sie neben Erhitzer, Kühler und Dampfbefeuchter ein Filter der Klasse B_2 sowie ein Aktivkohlefilter passierte. Anschließend wurde die Außenluft mit Umluft aus den klimatisierten Räumen gemischt und nach erneuter Passage eines B_2-Filters den Räumen zugeführt. Der Außenluftanteil betrug mindestens 10%.

Die Meßwerte lagen 3 m vor dem Aktivkohlefilter im Zuluftkanal, unmittelbar hinter dem Aktivkohlefilter und in einem klimatisierten Raum. Infolge der geringeren CO-Konzentration wurden 20 Hübe durchgeführt.

Da alle Messungen im Winter erfolgten, lag die Außentemperatur unter 10°C, die relative Feuchte betrug 50 bis 70%.

3. Ergebnisse:

Die folgenden Abbildungen zeigen nur einen Ausschnitt aus dem Meßprogramm.

Aus Abb.1 geht hervor, daß die Schwankungen der CO-Konzentration in der Tiefgarage relativ groß sind und bis zu 25 ppm über den Werten liegen, die am Ende des Abluftkanals gemessen wurden. Bei den dort gemessenen Werten muß eine Vermischung von Außenluft mit der Tiefgaragenabluft berücksichtigt werden. Eine Adsorption von CO an die Kanalinnenwände ist im Gegensatz zu SO_2 (4) unwahrscheinlich.

Die Abb.2 zeigt, daß die CO-Werte vor und hinter dem Aktivkohlefilter fast identisch sind, wenn man in die Beurteilung die große Standardabweichung der Meßmethode mit einbezieht. Die CO-Raumluft-Konzentrationen liegen häufig unter denen der übrigen Meßpunkte, da der Raum von Mischluft versorgt wird, die zum überwiegenden Teil aus den klimatisierten Räumen stammt.

Abb. 1 : CO - Messungen in einer Tiefgarage

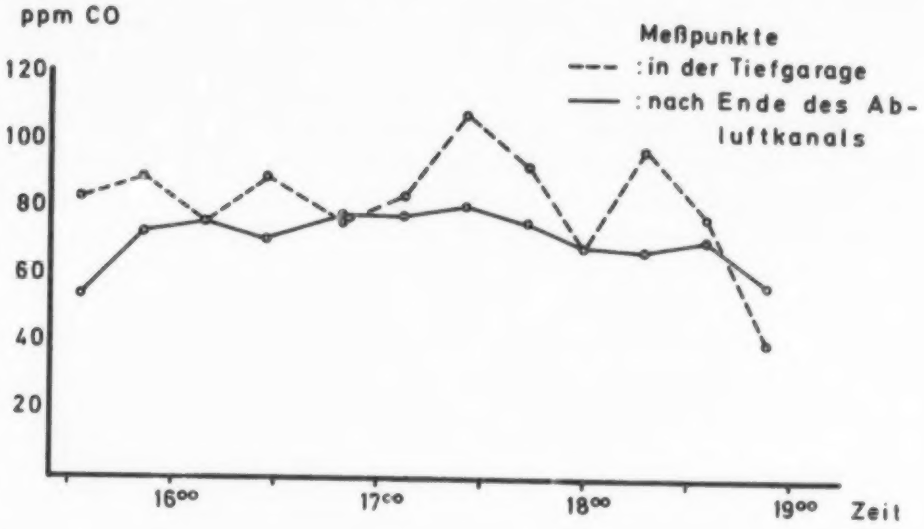
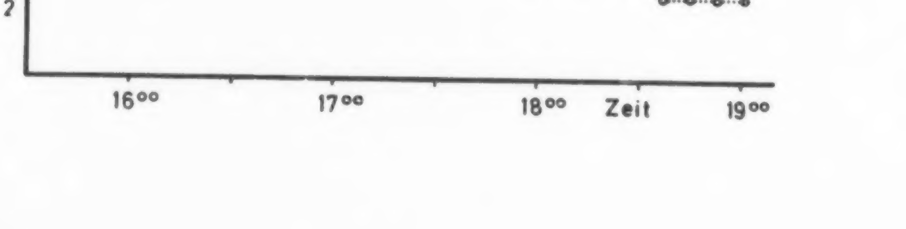


Abb. 2 : CO-Messungen in einem klimatisierten Gebäude



4. Schlußbetrachtung

Die Ergebnisse haben gezeigt, daß Kohlenmonoxid durch Gebläse, Mauerwerk, Dampfbefeuchtung, Faserfilter oder Aktivkohlefilter keine wesentliche Verminderung erfährt. YOCOM u. Mitarbeiter (6) kommen aufgrund eigener indoor-outdoor-Messungen von Kohlenmonoxid zu dem Schluß, daß die Innenluftkonzentrationen in klimatisierten Räumen (ohne die Art der Klimatisierung zu bezeichnen) die Außenluftkonzentrationen von Kohlenmonoxid genauer widerspiegeln als in natürlich belüfteten Räumen. Mangels einer leistungsfähigen Methode zur CO-Abscheidung durch herkömmliche lüftungstechnische Anlagen ist daher anzuraten, den Ansaugschacht klimatisierter Gebäude wegen der mit zunehmender Höhe abnehmenden CO-Konzentration (3) mindestens 40 m über Straßenniveau zu legen oder in Bereiche auszuweichen, die weniger CO-belastet sind.

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RECAPITULATION OF EXPOSURES AROUND A POINT SOURCE OF AIR POLLUTION

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ABSTRACT

The Salt Lake Valley offers a unique setting for observing relationships between the health parameters of the Community Health and Environmental Surveillance System (CHESS) and a gradient of human exposure to sulfur dioxide. Four communities in or near the Salt Lake Valley were chosen to represent an exposure gradient to sulfur dioxide, emitted primarily from a large copper smelter. The study communities, Magna, Kearns, Salt Lake City, and Ogden, are located approximately 5, 8, 13 and 35 miles from the smelter respectively.

Air monitoring sites were positioned approximately in the center of each study population. Total suspended particulates and their sulfate and nitrate fractions, sulfur dioxide, and nitrogen dioxide were monitored daily. Dustfall concentrations were measured monthly.

Arithmetic mean sulfur dioxide and suspended sulfate concentrations showed that Magna had the highest levels with Kearns, Salt Lake City and Ogden following in that order.

Past sulfur dioxide and suspended sulfate exposures were estimated from annual smelter emissions and currently measured levels and indicate that past exposures were considerably higher than present levels.

1. Introduction

Previous epidemiological studies, in urban areas, investigating sulfur dioxide effects have been confounded by mixed exposures to total suspended particulates and other pollutants. In the Salt Lake Valley, exposures to sulfur dioxide and suspended sulfates are primarily influenced by a large copper smelter west of the four selected study communities. The Utah CHESS study areas are situated in the north central part of the State of Utah and include Ogden, Salt Lake City, Kearns and Magna. These communities were selected on the basis of meteorological information, emission inventories and previous air quality measurements to provide an exposure gradient for sulfur dioxide with similar levels of other pollutants below the National Ambient Air Quality Standards.

2. Pollutant Measurement Techniques

For the Utah CHESS communities, the air monitoring sites were located within approximately 1.5-mile radius of the center of the human population under study.

Twenty-four-hour sulfur dioxide and nitrogen dioxide measurements were obtained with standard gas bubblers using the modified West-Gaeke[1] and Jacobs-Hochheiser[2] techniques respectively. High volume air samplers collected 24-hour samples of suspended particulate matter. For the sulfate and nitrate fractions of suspended particulate, turbidimetric and reduction diazo coupling methods were used respectively. The measurement of atmospheric particulate dustfall collected in a dustfall bucket over a month-long period provided an approximate gauge of the amount of environmental contaminants that precipitated out of the atmosphere on to the respective CHESS neighborhoods.

3. Results and Discussion

Table I summarizes the Utah CHESS 1971 annual averages for all pollutants. The National Ambient Air Quality Standards are shown for comparison. Annual average sulfur dioxide and suspended sulfate concentrations show that Magna had the highest levels with Kearns, Salt Lake City and Ogden, following in that order. Although Salt Lake City, Ogden and Kearns had similar average sulfur dioxide levels, Magna had the highest daily peak values. Daily sulfur dioxide peak values for Kearns were considerably lower than Magna, but higher than either Salt Lake City or Ogden.

Table I. SUMMARY OF UTAH CHESS 1971 ANNUAL AVERAGES FOR POLLUTANT CONCENTRATIONS

Pollutant	Ogden	Salt Lake City	Kearns	Magna	Standard[b]
Sulfur dioxide,[a] $\mu g/m^3$	8.0	15.3	21.7	61.8	80.0
Suspended sulfate,[c] $\mu g/m^3$	4.8	6.1	6.4	9.6	-
Total suspended particulate,[c] $\mu g/m^3$	66.5	70.9	38.2	53.9	75.0
Nitrogen dioxide,[a] $\mu g/m^3$	37.4	40.6	22.3	20.8	100.0
Suspended nitrate,[c] $\mu g/m^3$	2.0	2.4	1.7	1.3	-
Dustfall particulate,[a] $g/m^2/mo$	4.34	3.56	2.44	4.61	-

a. Annual arithmetic mean values

b. National Primary Ambient Air Quality Standard.

c. Annual geometric mean values.

The highest total suspended particulate concentration occurred in Salt Lake City followed by Ogden, Magna and Kearns in that order. Nitrogen dioxide and suspended nitrates exhibited similar gradients. Salt Lake City received the highest exposure while Ogden recorded slightly lower levels. Kearns and Magna had similar but considerably lower concentrations that the other two communities.

It should be noted that annual mean concentrations of total suspended particulates and nitrogen dioxide were below the National Ambient Air Quality Standards for all communities.

4. Past Exposure Estimates

Measured pollutant concentrations, of course, provide the most accurate data for use in epidemiologic studies. In the absence of measured values required for long-term studies; however, it is sometimes necessary to estimate past exposure levels.

Table II. ESTIMATED ANNUAL ARITHMETIC AVERAGE POLLUTANT CONCENTRATIONS FOR UTAH CHESS COMMUNITIES, 1940-1971.

Pollutant	Community	Concentration,[a] μg/m^3			
		1940-49	1950-59	1960-69	1971
Sulfur dioxide	Low (Ogden)	--	--	--	8
	Intermediate I (Salt Lake City)	--	--	(20)	15
	Intermediate II (Kearns)[b]	--	(50)	(33)	22
	High (Magna)	(234)	(142)	(95)	62
Suspended sulfates	Low	--	--	(4.8)	5.6
	Intermediate I	--	(11.4)	(7.5)	7.3
	Intermediate II	--	(10.4)	(8.8)	7.8
	High	(27.7)	(19.5)	(15.3)	12.4

[a] Parentheses indicate estimated values.

[b] Kearns, the Intermediate II community, was established in 1953.

Past exposures to sulfur dioxide and suspended sulfates were estimated from sulfur dioxide smelter emissions dating back to 1940. For each year the ratio of that year's sulfur dioxide emissions to the emissions for the year 1971 was calculated. This ratio was then multiplied by the 1971 annual averages for sulfur dioxide and suspended sulfate to give crude yearly past exposure estimates for sulfur dioxide and suspended sulfate levels respectively. These results are shown grouped by decades in Table II.

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RECAPITULATION OF METROPOLITAN AIR POLLUTION EXPOSURES ARISING FROM MOBILE AND STATIONARY SOURCES

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ABSTRACT

Measurements of previous air pollution exposures and continuing air monitoring surveillance in a study community provide an exposure basis for epidemiologic studies on the health effects of ambient pollution. Sulfur dioxide, total suspended particulate and dustfall measurements for the city of Chicago, Illinois, and for the Chicago-Northwest Indiana Metropolitan area have been obtained in recent years. Based on these measured values, it was possible to estimate past pollutant exposure in these areas for the period 1950-1970(1).

Limited data were available during the earlier years of the 1950-1970 period. A consistent correlation was found to exist between dustfall and total suspended particulates, and dustfall and suspended sulfates for those years when these measurements were available. Using this relationship total suspended particulate and suspended sulfate exposures were estimated from dustfall for those years when only dustfall was available. Sulfur dioxide was not correlatable to dustfall; however, limited data provided exposure estimates for 1960-1970.

The estimates were useful in determining an exposure gradient within the city of Chicago and across the entire area.

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1. Introduction

In order to carry out epidemiologic studies on the health effects of ambient pollution, it is important to have measurements of previous air pollution exposures for the community under study as well as continuing air monitoring surveillance. An epidemiologic study[2] conducted to determine chronic respiratory disease effects of combined exposure to particulates and sulfur oxides, required exposure estimates for two decades prior to 1970. Data were available from which to determine current and recent exposure; however, data between 1950 and 1960 were very limited. A method for providing exposure estimates during this time period, therefore, was required.

2. Pollution Sources

Mobile pollution sources include automobiles, trucks and airplanes. Stationary pollution sources include primarily power generating plants, residential, commercial and various industrial sources without dominance from any one specific type of product. Combined pollution effluents from these sources are continually influenced by changing climatological conditions creating complex exposures to area residents.

3. Exposure Methodology

A data search which included city, county, state and Federal sources was conducted. Air sampling methods and sampling frequency were analyzed for consistency. Graphical trends of individual pollutants were determined. Pollutant concentrations before and after implementation of control devices were examined. Meteorological models using available inputs (wind speed and direction, topography, source emission, source [stack] height, etc.) were compared with measured data. One model[3] available for the Chicago area was useful in determining sulfur dioxide distribution in the area from 1960-1970.

The above procedures were useful in determining estimates of exposure during the latter decade. Air monitoring data for the 1950-60 period were very limited. Except for annual particulate dustfall in Chicago, many data points were missing. Relationships between pollutants were computed from more recent years to provide reasonable estimates for missing data points. The annual arithmetic mean for Total Suspended Particulates (TSP) and the annual arithmetic mean for Dustfall were examined over time. Both revealed a similar trend of decreasing concentrations with time. A least squares fit of TSP (Y) versus Dustfall (X) gave the linear regression equation: Y= -49.5 + 14.4X and provided a correlation of r = 0.747. This approach indicated that Dustfall is a reasonable basis for estimating TSP; however, it did not account for the ratios changing with time. A second graph with TSP divided by Dustfall (Y) plotted against the corresponding year (X) was made which provided the linear regression equation: Y = 12.4 - .134X and r = .336. This ratio multiplied by the annual dustfall value was used for estimating annual TSP concentrations for 1950-1953.

Repeating this approach for suspended sulfates versus dustfall gave a least squares fit of Y = 3.40 + 1.276X with a correlation of r = .738. A plot of suspended sulfates/dustfall versus time yielded Y = 1.16 + .008X with r = .235. This technique was used for estimating suspended sulfates for 1950-1953.

A similar comparison between sulfur dioxide and dustfall data showed no consistent relationship. Data from a conductometric instrument was used to provide exposure estimates for 1960-1970.

4. Conclusions

Measured pollution levels provide the most accurate estimate of pollutant exposure in an area immediately surrounding the monitor. Emission inventories from point sources and traffic count of mobile source offer additional information from which to base meteorological models which can be used for larger area coverage.

In the absence of measured data for a given pollutant, weighted consideration can be given to major source emission levels, traffic changes, meteorological models and relationships between pollutants to provide past exposure estimates. Although the limitation of subjective analysis and extrapolating to earlier years is recognized, this provided a crude estimate of previous exposures in the Chicago area where measured data was unavailable. The exposure estimates indicated a definite pollution exposure gradient highest in east central Chicago and decreased radially toward the city boundary. Overall exposure in the suburbs was generally lower than exposure within the city, with the exception of sulfur dioxide. In some instances, sulfur dioxide exposure in the suburbs equaled or exceeded the city exposure, possibly as a result of point sources. Low exposures for non-urban areas, attributed to fewer sources per unit area, were verified.

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THE PROBLEM OF PASSIVE SMOKING IN MOTOR CARS

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ABSTRACT

Interest in measurement of concentrations of tobacco smoke in closed rooms has been stimulated by a growing concern over air pollution. Since 1969 a number of investigators have reported on measurements of tobacco smoke constituents, especially of the toxicological most important CO and nicotine. Measurements of the absorption of these compounds by nonsmokers were also reported. The situation in motor cars has not been intensively investigated so far.

Therefore, we carried out CO measurements in a motor car of the lower middle-class which was occupied with 3 smokers and one nonsmoker. Experiments were carried out in a wind-tunnel. Doors and windows of the car had been closed and the motor was off. At a relative-wind velocity of 0 and 50 km/h ventilation was varied. In one series of experiments the 3 smokers smoked a cigarette simultaneously following intervals, in total 6 or 9 cigarettes; in another series of experiments one smoker after another smoked a cigarette, in total either 4 or 6 cigarettes.

These experiments were completed by CO measurements in driving motor cars of different types. During a running time of 20 min. on a fixed route through Hamburg 2 x 2 cigarettes were smoked under conditions of ventilation as in the wind-tunnel experiments.

Results of our investigations may be summarized as follows:

1) *There was an increase of the CO level during smoking of cigarettes in a driving car.*
2) *This CO-level decreased in smokeless periods to ambient CO level within a few minutes.*
3) *Smoking without interruption led to an equilibrium concentration but not to a constant cumulation of smoke constituents in the air.*
4) *Absolute concentrations were depending on ventilation.*
5) *Only in a stationary, unventilated car the CO level constantly increased when smoking during the experimental period. However, this seems to be an unrealistic situation.*

Introduction

SRCH (1) observed that smoking of 10 cigarettes to a 5 mm butt length in an enclosed car standing in a closed garage caused CO levels up to 90 ppm. These cigarettes were smoked by 2 smokers within one hour. This study was done to clear up a murder. SEIFF (2) published results of investigations carried out in a stationary bus with running blower. Under "worst-case" conditions (all passenger seats occupied with smokers smoking 50% of the time, i.e. a 100% load factor for the bus with 43 seats - this situation was simulated by having one cigarette burning at each two seating positions all the time) he found a stable CO level of 33 ppm with an ambient level of 7 ppm about half an hour after the beginning of experiment. Under more realistic conditions (5 cigarettes burning all the time, simulating that 20% of the bus seats were occupied with smokers smoking 50% of the time) the CO-reading stabilized at 18 ppm after 42 min. Ambient CO level was found to be 13 ppm.

The objectives of our investigations were to study the influence of smoking and other circumstances, such as ventilation, air stream and ambient CO level, upon the CO concentration in motor cars (3,4).

Method

Experiments in the wind-tunnel* were carried out in a 4-door "European" motor car (55 PS) at a relative-wind velocity of 0 and 50 km/h. Windows and doors had been closed. Ventilation was varied as follows: Ventilation 1 = air jets closed, blower off. Ventilation 2 = air jets opened, blower off. Ventilation 3 = air jets opened, blower on. The car was occupied with 4 persons - only the driver was a nonsmoker. Smokers smoked either simultaneously at intervals or one after another. CO was measured with non dispersive IR (Harmann & Braun, Germany).

Experiments in driving motor cars were carried out in 9 different types of cars on a route of 15 km through Hamburg. Conditions of ventilation were the same as in the wind-tunnel experiments. During the course of experiment air samples were taken inside the motor car at 13 measuring points. Samples were analyzed immediately after return to our institute. CO was measured with non dispersive IR (Maihak, Germany).

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*carried out in collaboration with W. Liedl and D. Denker, Forschungsinstitut für Kraffahrwesen und Fahrzeugmotoren, University of Stuttgart, Germany

Table I: Wind-tunnel experiments: Mean CO level in a motor car occupied with 3 smokers and 1 nonsmoker. The smokers smoked simultaneously at intervals or one after another.

Speed km/h	Ventilation	Ambient Air ppm CO	Mean CO level in the car (ppm)						Decrease of CO level	
			3 cig	pause 20 min	3 cig	pause 10 min	3 cig		to ppm	after min
0	1	1	41	50	75	80	96		100	2.5
0	2	2	9	2	8	-	-		2	2
50	1	0	25	2	23	-	27		5	6
50	2	3	22	3	19	-	-		3	4.5
50	3	2	11	2	8	-	-		2	4
			Mean CO level in the car after smoking							
			1 cig	2 cig	3 cig	4 cig	5 cig	6 cig		
0	1	1.5	15	33	45	57	67	74	62	11.5
0	2	2.5	6	6	7	8	-	-	5	1.5
50	1	3.5	14	13	13	13	14	13	5	4.5
50	2	1.0	6	8	10	8	-	-	2	2
50	3	3.0	5	5	5	6	-	-	6	1

Table II: Mean CO level in motor cars occupied with 2 smokers and 2 nonsmokers. With smoking = 9 cars at ventilation 1 and 2 and 5 cars at ventilation 3 were tested. Without smoking = 23 rides. Between point 2 and 3 and between point 8 and 9 cigarettes were lightened. Smoking was stopped near to point 6 and between point 11 and 12.

Measuring point	Distance km	Mean speed km/h	Mean CO level (ppm)			
			non-smoking	smoking ventilation		
				1	2	3
1	0	0	0.8	0.5	0.8	1.0
2	0.95	33	3.2	1.7	2.5	2.3
3	1.95	39	3.8	11.3	12.0	11.4
4	2.40	17	6.0	17.9	15.9	13.6
5	4.60	77	2.3	21.1	9.9	6.0
6	7.10	88	1.1	7.8	3.9	3.3
7	8.10	47	1.3	4.0	2.0	1.5
8	9.90	42	3.6	4.5	2.6	2.3
9	11.50	46	5.6	11.3	7.9	8.0
10	12.30	33	5.3	24.3	18.4	18.9
11	13.40	40	4.8	21.4	15.7	12.0
12	14.80	35	2.5	9.3	6.9	5.6
13 (1)	15.35	22	4.5	7.6	5.7	3.9

The route through Hamburg included autobahn, main roads and by-streets. Two rides were carried out in the morning after rush-hour. During the first ride no cigarettes were smoked, during the second ride 2 of the 4 passengers smoked simultaneously 2 x 2 cigarettes. As blowers are installed in some motor cars only, it was not possible to carry out measurements at ventilation 3, i.e. air jets opened and blower on.

Results and Discussion

Results are summarized in table I and II. Experiments in the wind-tunnel demonstrated a quick increase of the CO concentration during the smoking period as well as a quick decrease of CO concentration after smoking 3 cigarettes simultaneously at intervals. The absolute CO level was depending on the ventilation. At a relative-wind velocity of 50 km/h ~25 ppm were measured in an unventilated car and ~10 ppm in a well-ventilated car. Only in an unventilated car at a relative-wind velocity of 0 km/h no sufficient decrease of the CO level was observed in the smoking intervals, and consequently the CO level increased during the second and third smoking period. Only under these circumstances the Threshold Limit Values were exceeded.

Corresponding results were obtained in experiments when one cigarette was smoked after another. Only in an unventilated car at a relative-wind velocity of 0 km/h there was an increase of the CO level after each cigarette smoked. In all other series of experiment a stable CO level was observed already during smoking the first cigarette.

Measurements in driving motor cars showed that our experimental results from one single motor car may be transferred to other cars. Just as in the wind-tunnel experiments the CO level in the car increased during the smoking period and decreased very quickly after smoking. When smoking the first two cigarettes, the car was running relatively fast. Accordingly, there was a better "natural" ventilation and the absolute CO value was a little lower than smoking the other two cigarettes.

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ANAESTHETIC VAPOUR POLLUTION IN OPERATING THEATRE ATMOSPHERES

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ABSTRACT

This paper describes part of a comprehensive investigation to examine the exposure of operating theatre staff to pollution of the atmosphere by halothane, trichloroethylene and methoxyflurane vapours as well as nitrous oxide.

The extent of atmospheric pollution in the operating theatre is determined by a continual, electron capture gas chromatographic system in which air samples from discrete predetermined locations in the theatre are analysed automatically at regular intervals. The influence of ventilation and scavenging systems on the pollution levels are important parameters. The advantages of a diffusion cell for the preparation of standard mixtures of anaesthetic vapours in air make this a useful technique for research in anaesthetics.

The results of some initial investigations are presented.

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1. Introduction

There is no doubt that pollution of the atmosphere in an operating theatre occurs through the discharge of anaesthetic vapours. It is important to know the extent of this pollution so that any harmful effects of chronic exposure can be examined and ways of reducing the contaimination can be investigated. However, there are many ways of measuring the concentrations of the vapours and of interpreting the results.

Several workers have taken air samples manually into syringes or plastic bags, but this approach can cause errors by leakage or adsorption of samples on surfaces. Nevertheless, the concept of measuring the distribution of the pollutants at different points in the theatre by 'snatch' sampling is useful. It does seem meaningless, however, simply to produce an average value of these results, particularly when a broad distribution of concentrations is found. Trapping the components in a large volume of air, followed by their analysis, is a more efficient way of obtaining an average concentration.

We consider that it is important to examine the distribution of anaesthetic vapours as well as the exposure levels of selected personnel in the environment. For this purpose the analysis of discrete samples is essential.

2. Techniques

2.1 Analysis

Gas chromatography is very useful for the separation and analysis of anaesthetics, but major problems concern the sampling technique and the presentation of the sample to the instrument for analysis. The system used in this study incorporates a multi-stream arrangement in which a pump draws samples from various sites within the operating theatre through nylon tubes to a gas sampling valve and then to a gas chromatograph (Hewlett Packard Model 5713). Each sample point can be selected automatically in turn for analysis to allow repeated, discrete sampling over long periods. This approach gives a reliable estimate of the distribution of anaesthetic vapours. For environments where halothane and trichloroethylene occurred together, a separation was obtained on a glass column (4.6m x 0.6cm o.d.) packed with silicone fluid, DC560, on Universal support (80-100 mesh). The carrier gas was Argon/methane (5%) flowing at 60 ml min^{-1} through the column maintained at 90°C. For the ultimate sensitivity to the halogenated agents, a pulsed electron capture detector is ideal; the linearity and stability of response are completely compatible with an automatic analysis system. Sampling through nylon tubes caused no losses by adsorption and the technique has the advantage that the tubes can be attached to personnel in order to monitor their immediate environments. The whole system is mobile to facilitate transport to operating theatres for on-site analysis.

2.2 Calibration

An accurate method for producing low concentrations of anaesthetic vapours is essential to give reliable analytical data. An ideal absolute calibration was carried out with a diffusion dilution cell as described by Savitsky and Siggia [1] and adapted by Robinson et al [2] . This technique relies upon the diffusion of vapour through a precision bore capillary tube into a gas stream to give a predicted concentration under established conditions. The reliability of the analyser system and the stability of its response were checked by this apparatus.

3. Discussion

The techniques described above are well known but hitherto have not been combined and applied to a study of air pollution in operating theatres. The system was used initially to investigate the pollution in a dental-outpatient, general anaesthetic department where relatively high levels of anaesthetic in the air were expected from the use of a semi-open breathing system. The sampling points were distributed throughout the surgery in positions of maximal activity and the overall distribution of positive measurements is shown in Figure 1. These values were surprisingly low by comparison with other published data and considering that air flow measurements indicated poor ventilation in the room. The distribution of the exposure levels of anaesthetists, however, was considerably wider and halothane levels exceeding $5.10^{-3}g.1^{-1}$ were recorded. Admittedly, the anaesthetists' inhalation zone is near to the expiratory valve of the nose mask, but it must also be significant that the flow studies indicated a stagnant zone of air where the anaesthetists work.

A complete interpretation of the data is proceeding and studies of other operating theatres are planned to give a more complete picture of the extent of air pollution by anaesthetic agents.

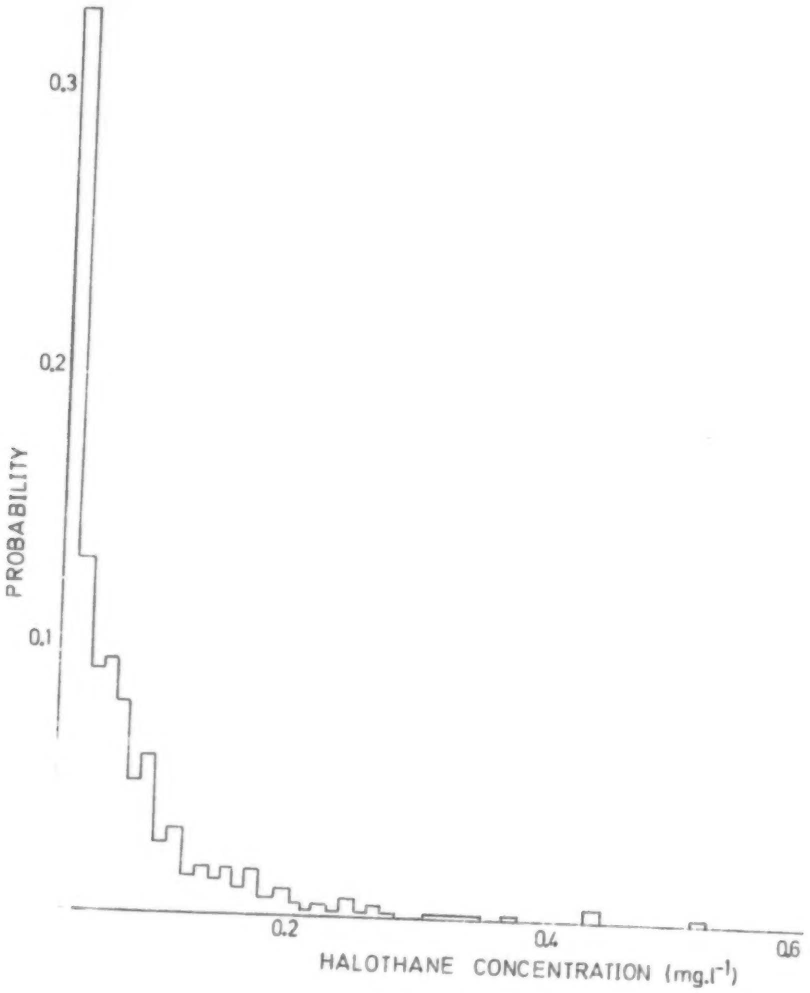

Figure 1 The Range of Concentrations of Halothane in the Air of an Operating Theatre. (Sample population 877).

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THE CONTRIBUTION OF ORGANIC LEAD COMPOUNDS TO TOTAL LEAD LEVELS IN URBAN ATMOSPHERES

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ABSTRACT

A sensitive adsorption technique for the determination of organic lead in urban air is described. Levels of organic lead as low as 0.01 μg m^{-3} may be determined with a 30 minute sampling period. The validity of the method has been tested, particularly with regard to possible adverse effects of other air pollutants upon the analytical accuracy. A summary of the levels of organic lead measured by this method in the London (U.K.) area is given, together with the levels of particulate lead measured concurrently. The highest levels of organic lead and the highest proportions of total airborne lead in the organic form were measured at a petrol station. A substantial reduction in levels of organic lead has been found upon moving away from a road or entering a building.

1. Introduction

Organic compounds of lead, used as petrol additives, are exhausted from motor vehicles largely in an inorganic, particulate form and abundant data are available on the levels of particulate lead in air. A very small proportion of the lead, however, is exhausted in an unchanged organic form, and this together with crankcase emissions and petrol evaporation contributes to the organic lead in urban air. Lead alkyl compounds normally exist in air in the vapour phase, and as they present a more difficult problem of measurement than the particulate form of lead little information regarding the exposure of the urban dweller to such compounds has been published. Some data have indicated that under certain circumstances, both for periods of short (Laveskog (1)) and long duration (Colwill and Hickman (2)), organic lead in urban atmospheres may account for in excess of 50% of total lead, although substantial variation between the results of different workers is apparent. In view of the known toxicological hazard associated with organic lead compounds, which is quite different from that due to particulate lead, and the uncertainty regarding levels of organic lead in air, further study appeared appropriate. Consequently a sensitive analytical procedure has been developed for the determination of organic lead in air which allows a rapid assessment of exposure.

2. Air Sampling and Analysis

Few methods have been reported for the determination of organic lead compounds at the very low levels found in urban air (Laveskog (1), Snyder (3), Purdue *et al*. (4)), and to date only one procedure has involved the use of short sampling periods in conjunction with modern instrumental techniques of analysis (Laveskog(1)). The method developed in this laboratory for the measurement of organic lead compounds in air, however, is readily applicable at levels as low as 0.01 μg m^{-3} involving a 30 minute sampling period (Harrison *et al*. (5)).

In essence, the air sampling procedure involves drawing approximately 0.02 m^3 of air through an adsorption tube packed with G.C. column packing material maintained at the temperature of liquid nitrogen (Figure 1), after prior collection of particulate lead by passage through a 0.22 μm Millipore filter which is subsequently analysed for lead. A short heating coil immediately preceding the adsorption tube maintains the enclosed tube at slightly above ambient temperature and ensures that any condensation of vapours occurs within the adsorption tube. After sampling, the

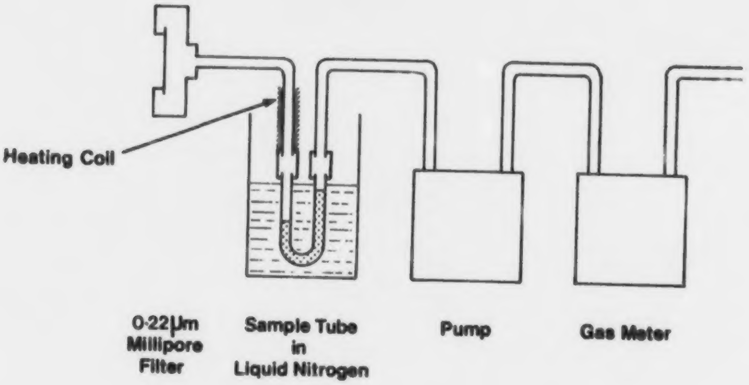

Figure 1 Air Sampling Apparatus

tube is stored immersed in liquid nitrogen and when required for analysis is inserted in an oven with its ends sealed by connection to a six-port switching valve (Figure 2). A nitrogen stream, passed initially through an identical blank tube, is diverted through the sample tube when the oven temperature stabilises at 130°. The eluted organic lead compounds are passed into the combustion air stream of an atomic absorption spectrophotometer set up for lead measurement. The analytical procedure, calibrated by the analysis of adsorption tubes dosed with an aliquot of a dilute toluene solution of a lead alkyl compound, has a detection limit of 0.2 ng of lead, corresponding to 0.01 ug m^{-3} of organic lead in a 0.02 m^3 sample of air.

2.1 Validity of the Method

The validity and precision of this procedure were tested initially in a number of ways (Harrison *et al.* (5)). A near quantitative collection efficiency was found for the sampling of known aliquots of tetramethyllead and tetraethyllead from air and the analytical procedure was found to be free from errors resulting from background absorption, or matrix effects due to trapped hydrocarbons and water.

2.1.1 The Effect of Other Air Pollutants upon the Analysis

It was subsequently suggested that other air pollutants, such as oxides of nitrogen, expected to be trapped during air sampling, might react with trapped organic lead compounds during air sampling or analysis,

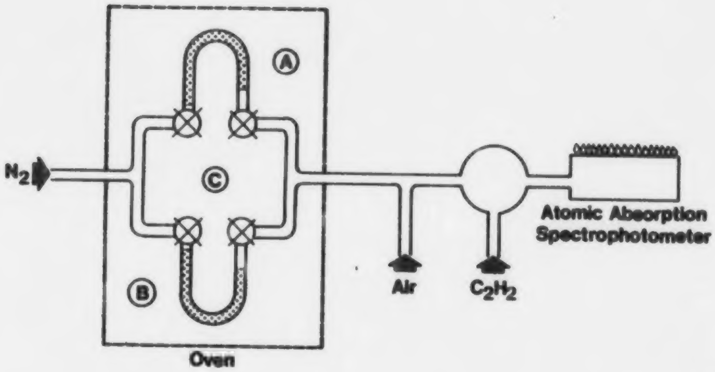

Figure 2 Organic Lead Analytical Apparatus

thereby converting volatile organic lead compounds into involatile lead compounds and hence introduce an error into the analytical result. Were this the case, it might have implications for other procedures involving the use of cooled sample tubes for the collection and determination of organic lead in air (Laveskog (1), Cantuti and Cartoni (6)), as well as for the procedure outlined above.

To investigate this problem urban air was sampled through two adsorption tubes connected in parallel (Figure 3). Prior to sampling, one tube was dosed with an aliquot of a lead alkyl compound, comparable in lead content to the anticipated quantity of organic lead to be collected from the urban air sample, whilst the other tube remained blank. Both tetramethyllead and tetraethyllead were used in this procedure. Air sampling was then performed in the normal way, the flows through the two tubes being equalised by use of the needle valves and rotameters (Figure 3). Both adsorption tubes were subsequently analysed in the usual manner. Analysis of 16 tubes used to sample air at 4 sites of widely differing levels of air pollution and airborne organic lead revealed a quantitative recovery of the dosed lead compounds to within the analytical error. Hence other air pollutants appear not to effect the analyses.

3. Levels of Organic Lead in Urban Air

Levels of organic lead and particulate lead collected concurrently were determined using the above procedure. Results were calculated both for the levels of organic lead in the air sampled, and the percentages of total

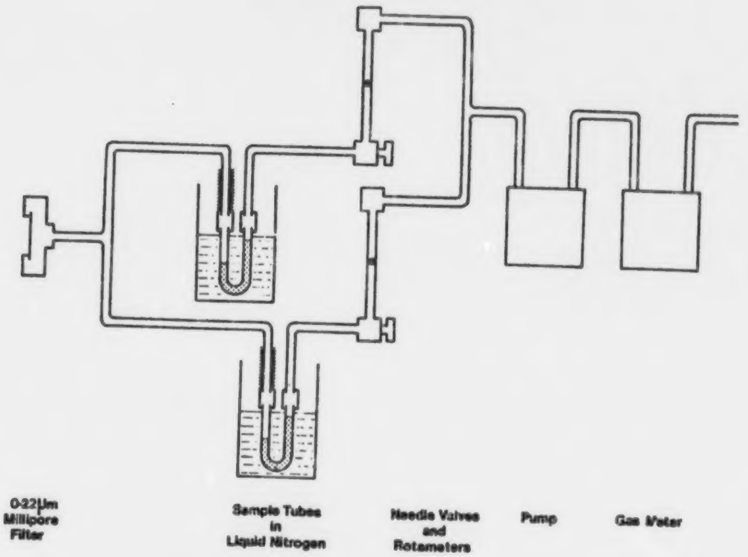

Figure 3 Apparatus for Sampling through Two Tubes in Parallel.

lead present in the organic form. The latter statistic is valuable as it is less dependent upon prevailing meteorological conditions and sampling site topography and is more reflective of source characteristics.

3.1 Kerbside Levels

In the London (U.K.) area measurements on streets of widely varying dimensions and traffic flow showed levels of organic lead of 0.04 - 0.11 µg m^{-3} with the percentage of lead in the organic form being 0.3 - 2.6%, the majority of results being in the region of 1 - 2%. Levels of particulate lead varied from 3.2 - 20.3 ug m^{-3}. Samples collected in a busy road tunnel showed particulate lead levels of 23.8 - 32.2 ug m^{-3} whilst organic lead levels remained around 0.02 µg m^{-3}; ca.0.1% of total lead.

Measurements taken on the forecourt of a busy London petrol station revealed organic lead levels in the range 0.21 - 0.59 ug m^{-3}, representing 3.9 - 9.7% of total airborne lead, whilst at a less busy petrol station out of the city an organic lead level of 0.07 ug m^{-3} (4.2% of total lead) was measured. Thus although, as anticipated, elevated levels of organic lead were found at petrol stations, particulate lead is still far the major form of airborne lead. It is clear that people working in close proximity to petrol pumps are exposed to significantly higher levels of organic lead than the population as a whole.

3.2 Levels at Greater Distance from the Road

Preliminary studies have indicated that levels of organic lead drop significantly with distance from the road, and upon entering buildings. In moving 20m from the kerbside of a busy London street the organic lead level was reduced from 0.07 to 0.01 μg m^{-3}, whilst particulate lead changed from 4.4 to 3.3 μg m^{-3}. Moving 10m further and into a building the organic lead level dropped to $<$0.01 μg m^{-3}, whilst the particulate lead level was 1.8 μg m^{-3}.

On a less heavily trafficked suburban road the levels of organic and particulate lead 2m from the kerbside were 0.03 and 0.7 μg m^{-3} respectively, whilst moving a further 4m and into a house the levels were reduced to 0.01 and 0.6 μg m^{-3} respectively. In view of the dilution with ambient air upon moving from the source of the lead, and the known instability of organic lead in air (Anon (7)) these results are readily explicable.

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ENQUETE PORTANT SUR LA CONSOMMATION FAMILIALE DE PESTICIDES DANS LES FAMILLES HABITANT DANS DE GRANDS ENSEMBLES DE LA REGION PARISIENNE

(METHODOLOGIE)

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RESUME

L'étude épidémiologique de la contamination par pesticides se justifie par le nombre minime de dosages en France parmi la population non exposée. Le propos supplémentaire de cette étude est d'essayer d'établir la corrélation entre les taux sanguins les plus élevés et l'origine de la contamination pour proposer des mesures préventives destinés à la diminuer.

Les diverses enquêtes s'attachent habituellement à préciser l'importance de l'apport alimentaire, certes prépondérant, mais non exclusif; la mesure de la consommation domestique d'insecticides ménagers peut faire apparaître un facteur favorisant de contamination.

ABSTRACT

This epidemiological study of pesticide levels is motivated by the very small number of determinations carried out in France among the unexposed population. A further aim of the study is to attempt to establish correlation between the highest blood levels and the source of the substances with a view to suggesting preventive measures to reduce the contamination.

Surveys of various kinds are usually designed to determine the quantities ingested with the food, this being certainly the most important, but not the only route of intake. Determination of the level of use of household insecticides in the home may bring to light a factor enhancing contamination.

MATERIEL HUMAIN

Les sujets étudiés ont été sélectionnés en fonction de trois critères :

1.1. - leur habitat urbain dans les immeubles de la banlieue parisienne, de façon à exclure l'exposition semi-professionnelle des maraichers et des propriétaires de jardin lors du traitement de leurs cultures, de façon aussi à obtenir une homogénéité relative dans les lieux d'achats des aliments pour laisser son importance au facteur d'utilisation de pesticides ménagers.

1.2. - leur métier, pour éliminer naturellement tout facteur professionnel d'exposition.

1.3. - leur coopération enfin, nécessaire pour répondre aux questions de l'enquête et accepter le prélèvement sanguin, la visite de l'enquêteur à leur domicile.

Aucune sélection n'a volontairement porté sur l'âge ou le sexe.

ENQUETE

Divers éléments sont précisés lors de l'interrogatoire :

2.1. - l'habitat antérieur, pour ne pas méconnaitre un séjour prolongé et récent dans une zone d'agriculture intensive riche en pesticides, et la date du dernier déménagement.

2.2. - la situation de l'appartement dans l'immeuble, car les étages inférieurs proches des espaces verts des résidences et le dernier étage possédant une terrasse jardin sont plus exposés aux produits de jardinage ; l'existence de pelouse à l'entour de la maison, la présence d'arbres dans les cours intérieures sont précisées.

2.3. - la présence de plantes.

2.4. - l'existence ou non d'animal domestique, chien, chat, oiseaux, souris, hamster, tortue, hérisson, ou autres ; les produits vétérinaires contiennent souvent des organo-chlorés (schampoing insecticide) ou des organo-phosphorés (vermifuges), les colliers insecticides pour chiens sont à base d'organo-phosphorés, le nettoyage et la désinfection des cages sont réalisés avec des produits multiples.

2.5. - la nature des parasites connus ou redoutés, dans l'appartement, sur les plantes, sur les animaux ; selon qu'il s'agit de moustiques, de mites, de mouches, de puces, de pucerons, l'insecticide utilisé diffère ; par exemple, les produits contre les cafards si résistants sont quasi toujours des organo-phosphorés.

2.6. - la description exacte des produits ménagers trouvés sur place le jour de la réalisation de l'enquête.

2.6. -1- les produits insecticides, sont notés en fonction de leur nom commercial, leur mode de présentation (bombe, plaquette, poudre...), le nom du fabricant, le lieu d'utilisation (cuisine avec son risque de pollution alimentaire, chambre avec contact journalier d'au moins 7 heures, salle de bains avec température plus élevée).

2.6. -2- les produits ménagers proprement dits, relevés selon les mêmes critères, correspondant aux détergents, détartrants ...., certains comme les désodorisants de lavabos, sont à base d'organo-chlorés type paradichlorobenzène.

2.6. -3- les produits utilisés pour traiter les plantes d'appartement.

Pour chacun de ces trois groupes, des précisions sont demandées sur les changements éventuels de marque par rapport aux mois précédents, ainsi que la notion d'incidents imputés par le public à leur manipulation. Pour cet interrogatoire, il est recommandé à l'enquêteur de demander la liste sans suggérer lui-même les noms commerciaux des produits les plus courants, pour ne pas influencer les ménagères.

Cette partie de l'enquête suppose le dépouillement dans un second temps de la liste de produits décelés sur place et obtenus par interrogatoire ; l'aide technique du Centre National d'Informations Toxicologiques, l'A.S.I.T.E.S.T., permet de connaitre la formule des produits utilisés.

2.7. les habitudes alimentaires dans le cadre familial sont précisées ; l'enquête s'attache à noter surtout deux point :

2.7. -1- le lieu d'achat : super-marché
magasin à succursales multiples
détaillant individuel,

car les circuits sommerciaux et la provenance risquent de différer.

2.7.-2- l'habitude de consommer cru : les légumes non épluchés (salades) les écorces de fruits frais.

2.8. la possession ou non d'une résidence secondaire qui naturellement majore le risque de contamination par l'emploi de produits pour protéger les charpentes, détruire les parasites dans la maison, traiter les plantes du jardin ; la fréquence de séjour (tous les week-end, les 15 jours, une fois par mois, tous les 6 mois, une fois par an) est appréciée.

2.9. le lieu de vacances annuelles comportant comme risques supplémentaires : le séjour en milieu rural, l'installation en zone chaude infestée de moustiques.

Cette enquête relativement détaillée n'a pas fait apparaitre de différences signficatives dans le mode d'alimentation, ce qui laisse son importance aux autres facteurs.

PRELEVEMENTS TOXICOLOGIQUES

L'enquête se poursuit par un prélèvement sanguin destiné au dosage des pesticides. Lors de la prise de sang sont notés systématiquement :

- le poids et la taille de l'individu,
- la nature des traitement médicamenteux en cours.

Le volume de sang prélevé sur héparine est d'au moins 10 ml. Son utilisation est double.

3.1. - une détermination et un dosage des insecticides organo-chlorés : 2 ml de sang sont élevés, après addition de 2 ml d'acétone et agitation, sur colonne de chromatographie garnie de sulfate de sodium anhydre et chargée de florisil sur une hauteur de 12 cm ; les 16 ml d'éluant ainsi recueillis sont étendus à 50 ml par une solution à 2 % de SO_4Na_2, puis extraits par 2 ml d'hexane, séchés sur du SO_4 Na_2 anhydride et injectés à raison de 5 µl en chromatographie gazeuse.

3.2. - un dosage du taux de cholinestérases sanguines, sériques et globulaires. La technique utilisée dérive de la méthode de Mitchell. Les érythrocytes, une fois lavés, sont maintenus à une température de 25° dans une solution riche en phosphates dans laquelle a été ajoutée de l'acétylcholine comme substrat. Les variations de pH, mesurées au pH mètre, exprimées en pH/h/25°, sont comparées au taux considéré comme normal dans notre laboratoire, 0,75 pour les cholinestérases érythrocytaires (0,70 pour les sériques).

L'analyse peut être répétée en cas de résultat nettement pathologique puisque le volume nécessaire est inférieur à 1 ml ; le lavage préalable des érythrocytes est une précaution supplémentaire contre les causes d'erreur bien que le résultat ne diffère guère.

Le dosage direct des organo-phosphorés dans le sang n'est pas envisagé dans le premier temps de cette étude.
Les résultats actuels témoignent d'une contamination relativement homogène de la population dans la banlieue parisienne. L'apparition éventuelle de divergences liées à l'utilisation différente de pesticides ménagers suppose :

- soit l'affinement de l'enquête pourtant déjà détaillée,
- soit l'extension de l'étude à un nombre plus élevé de sujets.

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• Contrat de Recherche : contamination des chaînes alimentaires.
Ministère de l'Environnement.

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APPLICAZIONE DELL'ANALISI SPETTRALE ALLO STUDIO DELLA DISPERSIONE DEGLI INQUINANTI ATMOSFERICI NELL'AREA DI VENEZIA

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RIASSUNTO

La presente ricerca ha cercato di individuare i meccanismi di dispersione degli inquinanti atmosferici nell'area di Venezia, partendo da dati rilevati al suolo.

Si disponeva delle medie orarie delle serie temporali di concentrazione di SO_2 rilevate per un mese e mezzo in diverse stazioni di monitoraggio, sia nell'area industriale che a Venezia stessa, e dei dati di velocità e direzione del vento raccolti in due stazioni meteorologiche.

Utilizzando l'analisi di Fourier, sono state evidenziate le caratteristiche spettrali delle serie temporali di concentrazione e di velocità e componenti orizzontali del vento al suolo.

Si conta di ottenere tutta una serie di ulteriori informazioni effettuando l'analisi di coerenza e fase su diverse coppie di serie temporali di concentrazione e crosscorrelando i dati di concentrazione con quelli meteorologici.

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ABSTRACT

This research deals with the evaluation of the atmospheric dispersion mechanism of pollutants in the Venice area in connection with wind-speed and direction patterns at ground level.

Disposing of six series of continuous records of SO_2 *concentration, collected at different fixed points in the industrial area as well as in Venice itself, the Fourier analysis was applied to hourly averaged data in order to obtain the spectral properties of the modulations of* SO_2 *concentration.*

1. Introduzione

Se ci si pone l'obiettivo di indagare sulla dinamica nel tempo e nello spazio del campo di concentrazione di un inquinante atmosferico, si incontrano subito notevoli difficoltà quando si voglia entrare nel dettaglio degli effettivi processi fisici che evolvono nell'atmosfera. Le difficoltà diventano praticamente insormontabili quando si vogliano studiare aree caratterizzate da forti disomogeneità superficiali: in tali condizioni si dimostra inadeguata gran parte della modellistica oggi disponibile, nè migliori risultati si ottengono cercando di risolvere le equazioni del moto, date le notevoli complessità che si incontrano nella loro integrazione.
Una possibile alternativa è quella di ricavare informazioni sulla dinamica dei fenomeni fisici in esame direttamente dai dati sperimentali, mediante l'utilizzazione di opportune tecniche di analisi. In tal senso va intesa l'applicazione delle tecniche di analisi spettrale allo studio del trasporto e della diffusione degli inquinanti atmosferici (M. Tilley e G. Mc Bean, 1973). Tali tecniche permettono di scomporre il fenomeno, per quanto complesso, nei processi elementari che lo compongono e di determinarne l'importanza relativa.
In questo lavoro, l'analisi spettrale è stata applicata allo studio dell'influenza dei fenomeni meteorologici a mesoscala sul trasporto e la diffusione di SO_2 sull'area di Venezia.
L'area di Venezia si presenta particolarmente valida per la sperimentazione di questo tipo di metodologia. In essa, infatti, sono presenti notevoli discontinuità superficiali (terra-mare, zona industriale, zona urbana, zona rurale) che danno luogo a fenomeni meteorologici a mesoscala particolarmente complessi, interessanti sia la circolazione che la struttura dei bassi strati dell'atmosfera (Lyons, 1973).

2. Dati utilizzati

I dati di concentrazione utilizzati sono quelli relativi ai livelli di SO_2 rilevati dalla rete per il controllo della qualità dell'aria nella zona di Venezia. Tale rete, realizzata dalla Tecneco SpA per conto dell'Istituto Superiore di Sanità e dell'ENI, consta di 24 analizzatori in continua Philips 9700 che campionano a una altezza di 4 m dal suolo.
Per questo studio, sono state utilizzate le medie orarie dei dati raccolti, nel periodo 1 febbraio - 14 marzo 1973, dalle 6 stazioni di fig. 1. Infatti, a quella data, delle altre stazioni alcune non erano state ancora installate, altre avevano avuto dei periodi relativamente lunghi di non funzionamento per manutenzione.
Come dati meteorologici, sono stati utilizzati i dati orari di direzione e velocità del vento, mediati sui dieci minuti precedenti l'ora di attribuzione, rilevati nelle stazioni di Tessera, del Servizio Meteorologico dell'Aeronautica Militare, e dell'Ospedale a Mare (stazioni A e B di fig. 1).
Tali dati sono relativi al periodo 1 febbraio - 14 marzo 1973.

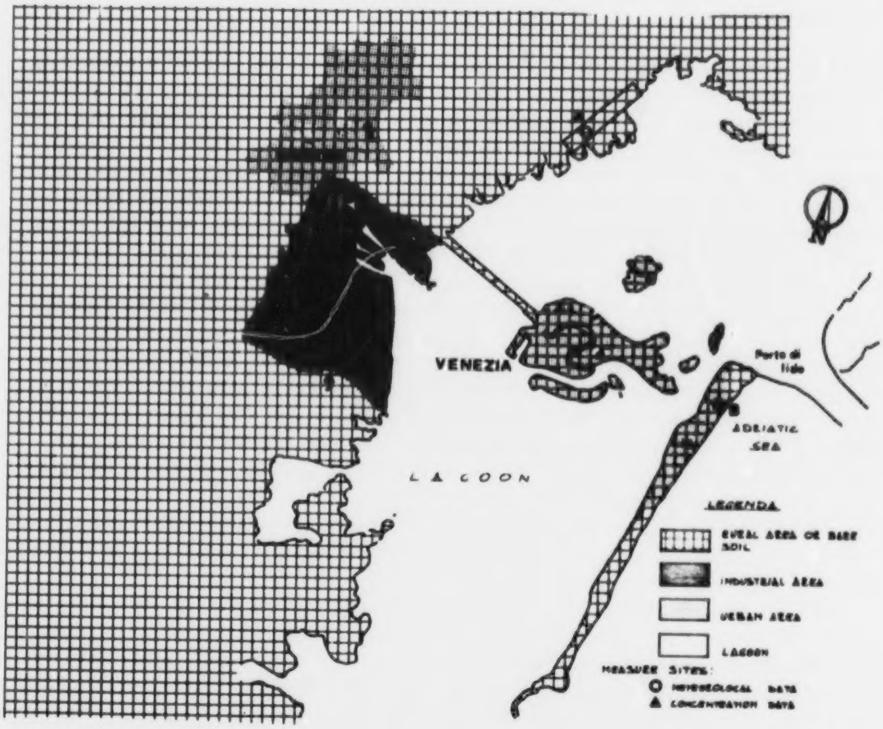

Fig. 1. Map of the Venice area

3. Metodo di analisi

Per le serie temporali delle concentrazioni di SO_2 e del modulo e delle componenti orizzontali della velocità del vento, sono state calcolate le funzioni di autocovarianza, a ritardi variabili da 0 a 200 ore, e le relative trasformate di Fourier, nel campo di frequenza tra 0.005 e 0.5 h^{-1}. Gli algoritmi usati sono in Jenkins Watts: "Spectral analysis and its applications" (1968). La finestra spettrale usata è quella di Bartlett; comunque, da prove effettuate, si è verificato che la forma degli spettri non cambia in modo apprezzabile al variare del tipo di finestra. L'effetto di "aliasing" sugli spettri dei dati della concentrazione di SO_2 è trascurabile poichè i dati sono mediati sull'ora. Per i dati di vento, mediati sui dieci minuti precedenti l'ora di attribuzione, si è proceduto a filtrare dalle serie temporali le componenti con periodo inferiore a 3 ore. L'intervallo di confidenza dell'80% sull'ampiezza degli spettri va da + 90% a - 40% dell'ampiezza calcolata.

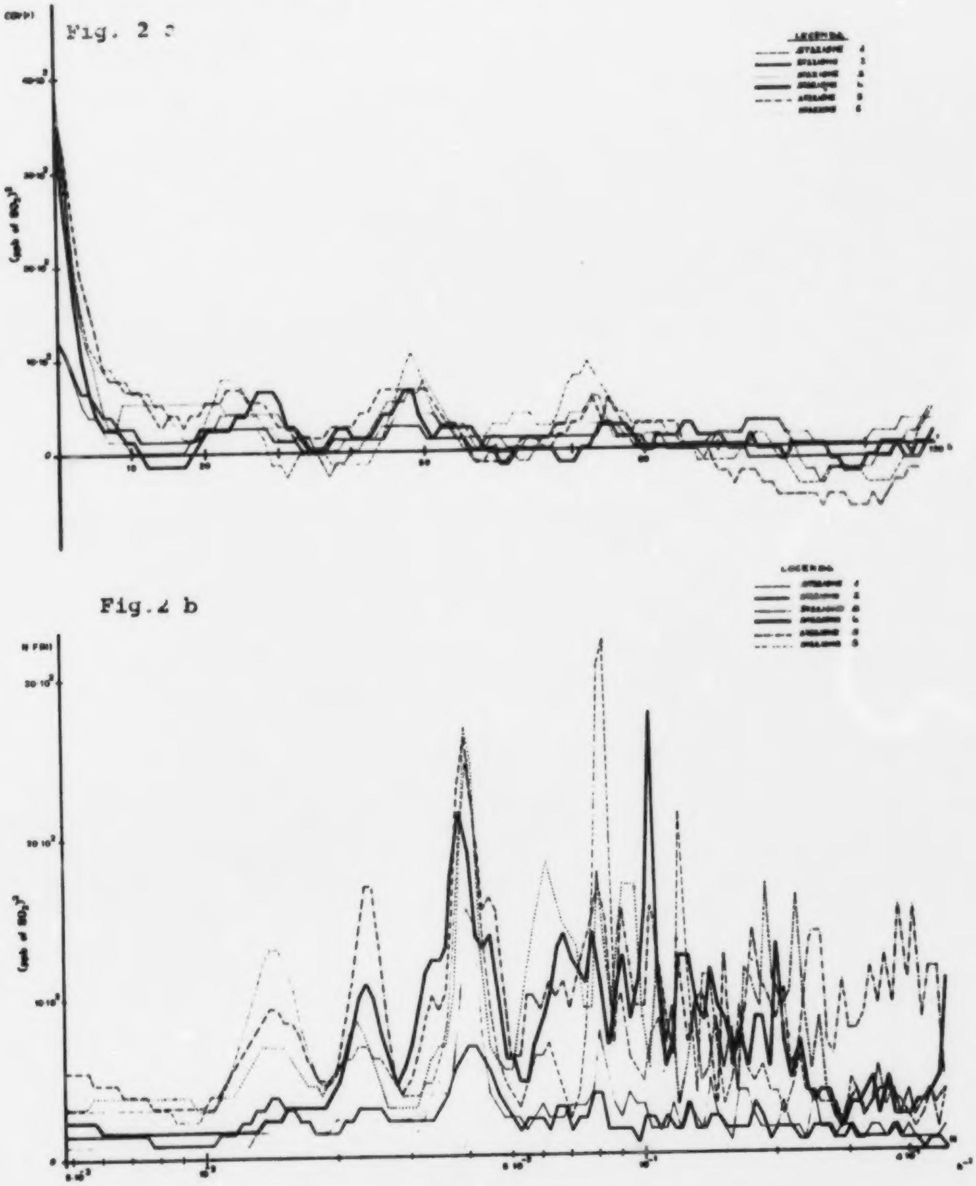

Fig. 2 a b-Autocohovariance (a) and power-specturm (b) of SO_2 concentration time series at the six monitoring stations indicated in fig. 1. In the power-spectrum the bandwidth is 0.0075 h^{-1}.

Fig. 3 a

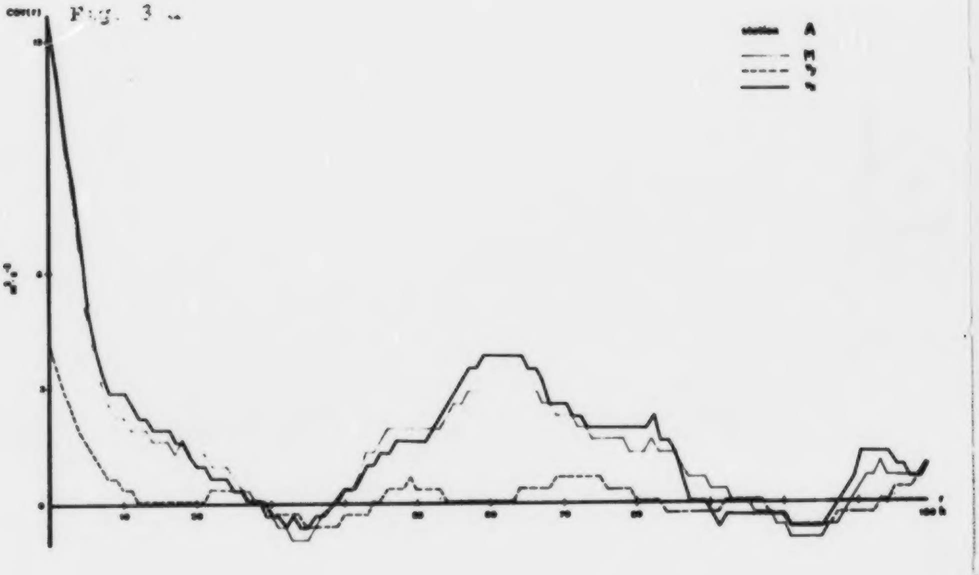

Fig. 3 b

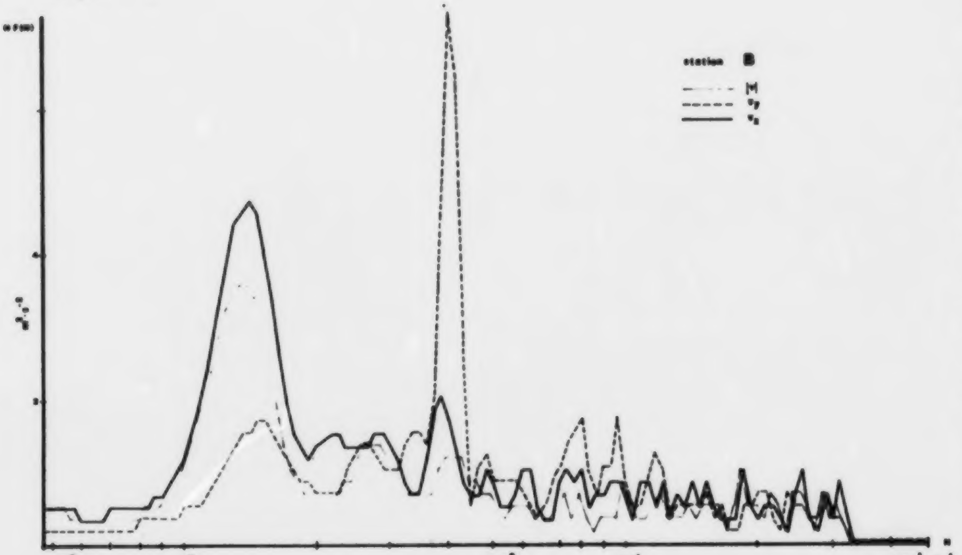

Fig. 3 a,b - Autocohovariances (a,b) and power-spectra (c,d) of time series of wind-speed ($|V|$) and -horizontal components (northwards v_y and eastwards v_x). A and B stations refer to fig. 1.
In the power-spectra the bandwidth is 0.0075h $^{-1}$.

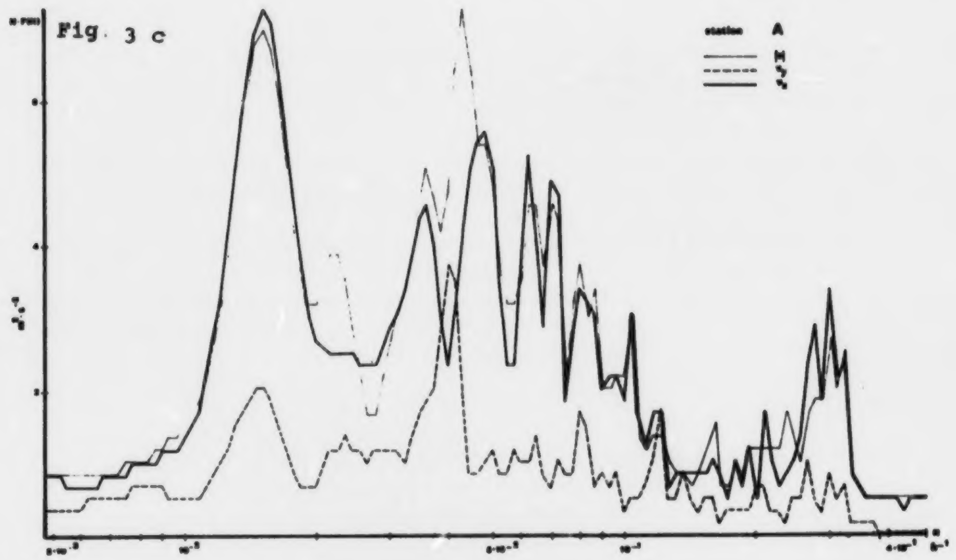

Fig. 3 c

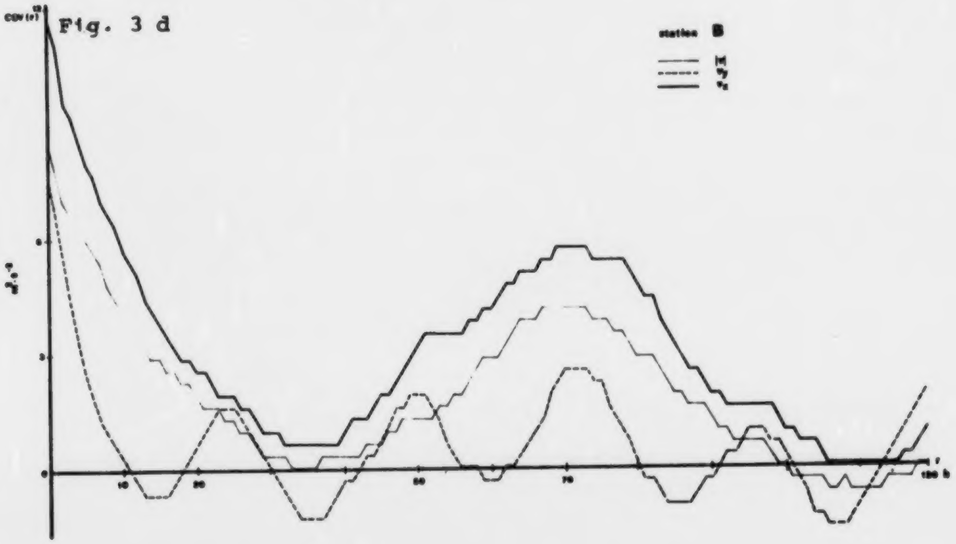

Fig. 3 d

ig. 3 c,d - Autocohovariances (a, b) and power-spectra (c, d) of time series of wind-speed (|v|) and -horizontal components (northwards v_y and eastwards v_x). A and B stations refer to fig. 1. In the power-spectra the bandwidth is 0.0075 h^{-1}.

4. Risultati

Poichè lo studio è in corso di completamento, sono stati riportati solo alcuni risultati preliminari. Nella fig. 2, sono riportate le funzioni di autocovarianza e gli spettri di potenza delle serie temporali della concentrazione di SO_2 rilevate nelle sei stazioni di misura.
Nella fig. 3, sono riportate le funzioni di autocovarianza e gli spettri di potenza del modulo e delle componenti orizzontali della velocità del vento, rilevate al suolo nelle stazioni A e B.
Negli spettri di potenza della concentrazione, sono evidenti le righe diurne, semidiurne e inerziali. Le righe con periodo attorno a 72 e 48 ore sono presumibilmente dovute al passaggio di perturbazione sulla zona di Venezia. Tale interpretazione è confortata da un esame qualitativo delle carte meteorologiche relative al periodo in esame.

5. Prospettive

Considerando gli spettri di potenza delle concentrazioni di SO_2 e quelli di velocità del vento, particolarmente interessante appare la diversità nei due casi dei pesi delle armoniche di periodo di circa 48 e 72 ore rispetto all'integrale dello spettro. Tale diversità di peso rende evidente la necessità di cercare un'interpretazione fenomenologica dell'influenza dei moti atmosferici a piccola energia (effetti inerziali, maree atmosferiche, ...) sui fenomeni di inquinamento atmosferico da sostanze in fase gassosa.
Dall'analisi degli spettri di fase delle serie temporali di concentrazione di SO_2 sembrano emergere indicazioni sulla struttura del regime di brezza nell'area considerata. Tale analisi è ancora in corso, insieme a quella sulla coerenza spaziale.

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STUDIO E VALUTAZIONE DEGLI EFFETTI DELL'INQUINAMENTO AMBIENTALE SULLA SALUTE DELL'UOMO ATTRAVERSO SIMULAZIONE CON MODELLI BIO-INGEGNERISTICO-CHIMICI

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RIASSUNTO

Sulla base dei più recenti studi a livello interdisciplinare che si collegano anche alle applicazioni biomediche dell'ingegneria chimica si propone un modello bio-ingegneristico chimico per la correlazione fisico-matematica esposizione-effetto ai fini della valutazione dell'inquinamento ambientale sulla salute dell'uomo.

Il modello è basato sulla applicazione della ben nota analisi compartimentale già con successo sperimentata nello studio della distribuzione, effetti e tollerabilità dei farmaci nel corpo umano concepito come uno o più reattori biochimici in serie-parallelo.

Il modello tiene conto al contempo dei principali parametri significativi ai fini degli effetti presunti o osservati sullo stato di salute dell'uomo quali: la concentrazione dell'inquinante, il tempo di esposizione, le caratteristiche intrinseche del soggetto esposto e per ciascun tipo di inquinante.

Il modello costituisce una alternativa di più rapida informazione, ad altri a tutt'oggi adottati di tipo epidemiologico e statistico e sembra si possa ben prestare all'interpretazione

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delle alterazioni fisiologiche e del comportamento dell'uomo in seguito ad esposizione ad inquinanti.

Esso inoltre è un'utile risorsa per valutazioni e previsioni significative sugli effetti: sinergici, antagonisti e addizionali degli elementi inquinanti sia a breve che a lungo termine.

ABSTRACT

On the basis of the most recent interdisciplinary studies concerning the biological and medical applications of chemical engineering, ideas have been put forward for a mechanical biochemical model designed to provide physical and mathematical correlations of exposure and effect, to assess the impact of environmental pollution on human health.

The model is based on the familiar analytical techniques already successfully tested in studies on distribution, effects and acceptable levels of drugs in the human body, and is in the form of one or more biochemical reactors in parallel series.

The model is designed to provide simultaneous measurements of the most important parameters indicating suspected or observed effects of pollution on human health, such as pollutant concentration, duration of exposure, and intrinsic characteristics of the exposed subject, relating these to the type of vehicle (atmosphere, water, food, noise), for each type of pollutant.

The model represents a faster-working alternative to the other epidemiological and statistical methods used so far, and it could well provide an excellent means of interpreting physiological and behavioural changes in man as a result of exposure to pollutants. Moreover, it provides a useful means of monitoring and making significant estimates of the synergic, antagonistic and cumulative effects, both short and long-term, of various pollutants.

1.Introduzione

Quando un gas tossico è presente nell'atmosfera e viene respirato dall'uomo si stabilisce una certa velocità di assorbimento attraverso le membrane alveolari entro il sangue polmonare prodotta da una differenza di concentrazione tra l'aria e il sangue.

Nella generalità dei casi i gas inquinanti non vengono metabolizzati e escreti attraverso le normali vie, ma sono eliminati quasi interamente attraverso i polmoni da cui vengono assorbiti (1).

Il trasferimento netto dagli alveoli al sangue è inizialmente rapido e quindi progressivamente diminuisce fino a che non si raggiunge un equilibrio.

Se c_s è la concentrazione di inquinante nel sangue, c_a quella alveolare si avrà per uguali volumi di sangue e aria a contatto:

$$\frac{dc_s}{dt} = k_1 c_a - k_2 c_s \qquad (1)$$

e poichè in prima approssimazione si suppone costante la concentrazione alveolare (c_a=cost) si può considerare il fenomeno come un assorbimento di ordine zero ed una eliminazione del 1° ordine (2).

All'equilibrio si può scrivere:

$$k_1 c_a = k_2 \bar{c}_s \qquad (2)$$

$$\frac{c_s}{c_a} = \frac{k_1}{k_2} = S \qquad (3)$$

Dove S è la solubilità del gas inquinante nel sangue. Sostituendo nella (1) il valore di k_1 dato dalla (3), il valore di c_a dato dalla (2) e chiamato f il rapporto $c_s/\bar{c}_s$ tra la concentrazione nel sangue istantanea e quella all'equilibrio, la (1) diventa:

$$\frac{df}{dt} = k_2(1-f) \qquad (4)$$

che risolta da:

$$1 - f = e^{-k_2 t} \qquad (5)$$

La Fig. 1 è la espressione grafica della (5) e da essa per vari tipi di inquinanti caratterizzati da diverso S e k_2, nota la concentrazione alveolare si può ricavare la concentrazione

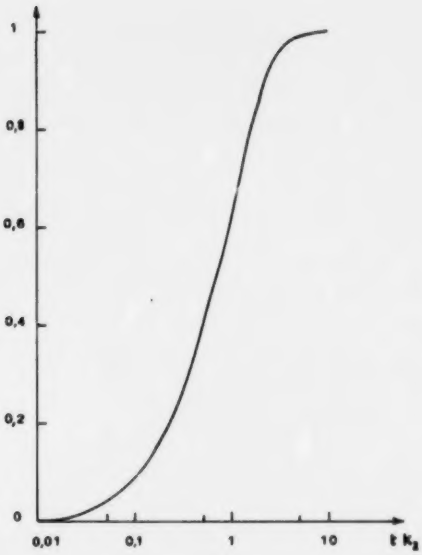

Fig. 1. Andamento del rapporto $c_s/\overline{c}_s=f$ in funzione del parametro adimensionale k_2t.

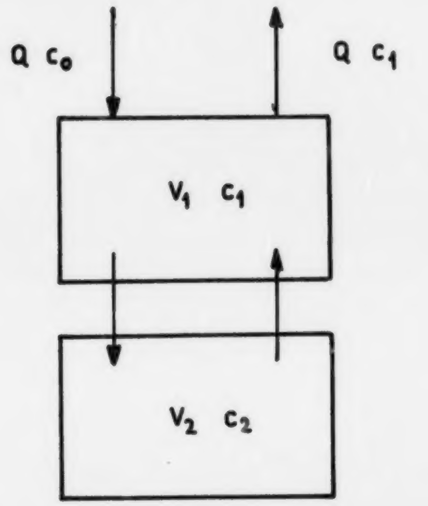

Fig. 2. Modello a 2 compartimenti per il sistema aria alveolare -frazione acquosa del corpo umano.

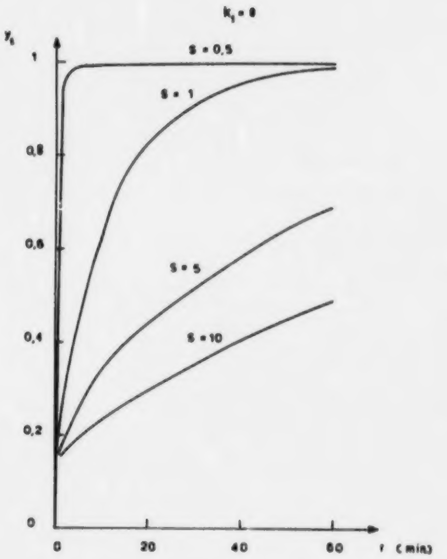

Fig. 3. Andamento della concentrazione alveolare di gas tossico (rispetto all'equilibrio) per gas gacilmente diffusibili $k_1=8$.

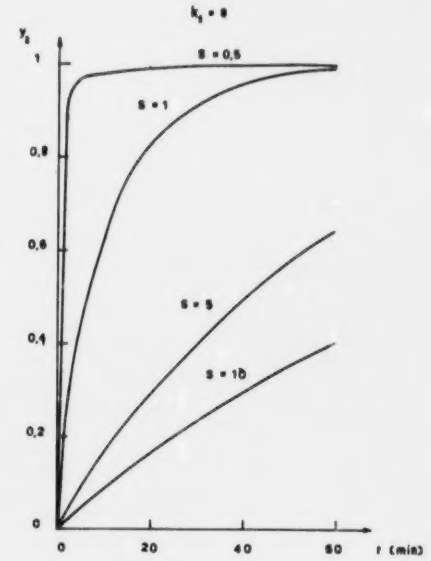

Fig. 4. Andamento della concentrazione di gas tossico nella frazione acquosa del corpo umano (rispetto all'equilibrio) per gas facilmente diffusibili $k_1=8$.

nel sangue e quindi per ogni tipo di inquinante prevedere gli effetti che esso avrà sul corpo umano.

In un approccio di seconda approssimazione occorre tener conto che la c_a raggiunge il valore della concentrazione atmosferica dell'inquinante solo dopo un certo tempo dipendente essenzialmente dalla solubilità dell'inquinante nel sangue in particolare, ed in generale nella frazione acquosa del corpo umano.

2. Modello a due compartimenti

Per tale caso più generale viene proposto un modello a due compartimenti che tiene conto oltre che del volume di sangue o frazione acquosa, anche del volume polmonare. La Fig.2 schematizza il modello (3,4,5,6).

Le equazioni che lo descrivono sono:

$$v_1 \frac{dc_1}{dt} = -k_1 v_1 c_1 + k_2 v_2 c_2 + Q(c_\circ - c_1) \qquad (6)$$

$$v_2 \frac{dc_2}{dt} = v_1 k_1 c_1 - v_2 k_2 c_2 \qquad (7)$$

dove v_1 e v_2 sono i volumi rispettivamente polmonare e del sangue, c_1 e c_2 le concentrazioni di gas tossico nei due compartimenti, $c_\circ$ la concentrazione esterna ai compartimenti, k_1 e k_2 costanti di diffusione attraverso la membrana alveolare, Q la portata di aria ai polmoni (lt/min).

All'equilibrio si ha : $c_{1\infty} = c_\circ$ e $c_{2\infty} = \dfrac{c_2}{c_\circ \frac{v_1}{v_2} S}$

Le (6) e (7) si possono riscrivere in termini di:

$y_1 = \dfrac{c_1}{c_{1\infty}}$ e $y_2 = \dfrac{c_2}{c_{2\infty}}$ per cui:

$$\frac{dy_1}{dt} = -(k_1 + \frac{Q}{v_1}) y_1 + k_1 y_2 + \frac{Q}{v_1} \qquad (8)$$

$$\frac{dy_2}{dt} = k_2 y_1 - k_2 y_2 \qquad (9)$$

Si tratta di un sistema di equazioni differenziali lineari di 1° grado che risolto con le condizioni iniziali $y_1=0$ e $y_2=0$ per $t=0$ conduce a:

$$y_1 = 1 - \frac{1}{k_2(r_2 - r_1)} \left[r_2(k_2 + r_1) e^{r_1 t} - r_1 (k_2 + r_2) e^{r_2 t} \right] \qquad (10)$$

$$y_2 = 1 - \frac{1}{r_2 - r_1} \left[r_2 e^{r_1 t} - r_1 e^{r_2 t} \right] \qquad (11)$$

$$\text{dove} \quad r_{1,2} = -\frac{1}{2}(k_1 + k_2 + \frac{Q}{v_1}) \pm \frac{1}{2} \sqrt{(k_1 + k_2 + \frac{Q}{v_1})^2 - 4 k_2 \frac{Q}{v_1}} \qquad (12)$$

Riportate in grafico (Figg.3,4,5,6) le (10) e (11) mostrano l'andamento delle concentrazioni di gas tossici in funzione del tempo per diversi tipi di gas ovvero per differenti valori di S e k_2 e nei due compartimenti scelti ovvero i polmoni e la frazione acquosa del corpo umano.

Come si può vedere dalle curve e ricavare analiticamente dalle (10) e (11) per i gas poco solubili dopo breve tempo la concentrazione negli alveoli raggiunge il valore di equilibrio

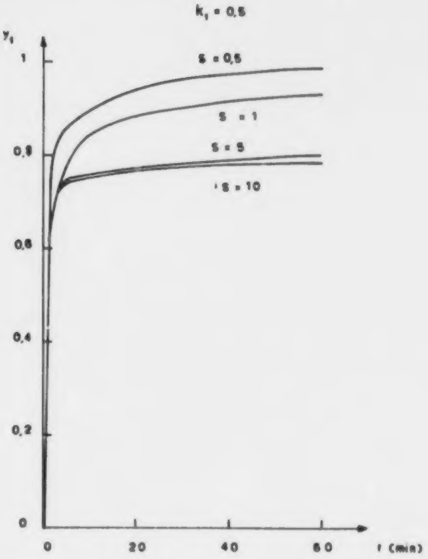

Fig. 5. Andamento della concentrazione alveolare di gas tossico (rispetto all'equilibrio) per gas poco diffusibili k_1=0,5.

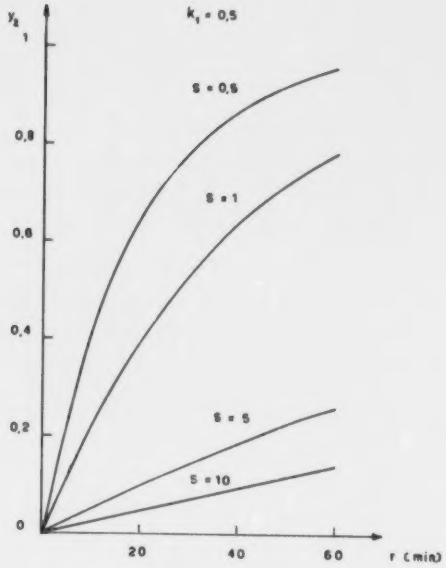

Fig. 6. Andamento della concentrazione di gas tossico nella frazione acquosa del corpo umano (rispetto all'equilibrio) per gas poco diffusibili k_1=0,5.

c_o e identicamente la concentrazione nella frazione acquosa raggiunge il suo valore di equilibrio in tempi piuttosto brevi.

Una situazione opposta è fornita dai gas ad alta solubilità per i quali l'equilibrio, nei due casi di alveoli e frazione acquosa, viene raggiunto in un tempo piuttosto lungo.

Il modello qui proposto può costituire una alternativa di più rapida informazione e quanto meno un utile ausilio ad altri a tutt'oggi adottati di tipo epidemiologico e sembra si possa prestare all'interpretazione delle alterazioni fisiologiche e del comportamento dell'uomo in seguito ad esposizione a gas tossici.

Gli Autori ringraziano il Prof. F.L. Petrilli per l'attenzione rivolta al presente lavoro e per gli utili suggerimenti critici ricevuti.

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A STATISTICAL ANALYSIS OF THE AIR POLLUTION DATA IN CONNECTION WITH THE METEOROLOGICAL CONDITIONS

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ABSTRACT

The pollution in the planetary boundary layer (PBL) with a height of about 1 km is investigated. Under conditions of stationarity and a horizontal homogeneity of the underlying surface the turbulent state in PBL is fully determined by the following external to PBL parameters: Rossby's number, the external parameters of thermal stratification and two external parameters of the baroclinicity. These parameters may easily be determined by the synoptic information. In the work it is looked for the relation between these representative for the diffusion process parameters and the data on the air pollution in different cities for a few year period of observation. It is shown that there exists a close relation between the external to PBL parameters and the air pollution.

These investigations give a possibility by data on the numerical weather forecast to predict the cases of strong air pollution, especially important for the industrial city regions since the necessary preventive measures can be duly undertaken.

1. Introduction

Meteorological conditions influence considerably the air pollution. Once studied this relationship enables us to predict the pollution by means of weather forecasts and when necessary to take in good time the required preventive measures. When statistically evaluating the air pollution data it is necessary to define the meteorological parameters on which it solely depends. Studies of relations of arbitrary meteorological conditions is inadequate. We are going to investigate the pollution in the planetary boundary layer (PBL). That is the layer with height of the order of 1 km above earth surface and naturally the pollution in it is of the greatest practical interest.

2. Representative meteorological parameters

The air pollution depends on the turbulent state: wind profile, coefficients of turbulent exchange etc. Let us assume conditions of stationarity and barathropy. The contemporary conceptions concerning the structure of PBL (crf. [1]) show that under these conditions the turbulent characteristics depend solely on the following dimensionless parameters

$$R_o = \frac{V_g}{fZ_o} \quad \text{surface Rossby number} \qquad (1)$$

$$S = \frac{g}{\bar{T}} \cdot \frac{T_H - T_o}{f\, V_g H} \quad \text{external parameter for thermal stratification} \qquad (2)$$

where V_g is the geostrophic wind which could be assumed to be equal to the wind of the top of PBL, f - Coriolis parameter, Z_o - roughness length of the order of several meters for a town, g - acceleration of gravity, $\bar{T}$ - the mean potential temperature, $T_H - T_o$ - the difference between the potential temperatures of height H and Z_o since both external parameters (1) and (2) are fully responsible for the turbulent state they must solely define the diffusion process in the PBL (crf. [2]). If we assume that the sources

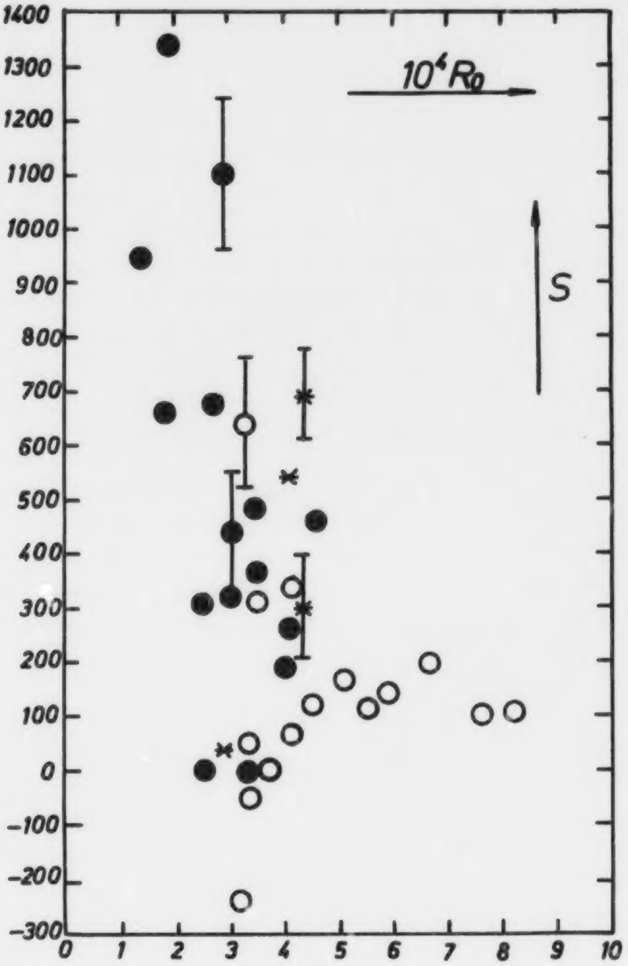

Fig.1 The dependence of air pollution data on the meteorological parameters R_o, S. ● ✱ o , strong, average and slight pollution, respectively.

of pollution around a particular measurement station do not change and have constant strength

$$\frac{b}{b_m} = F(R_o, S, K) \qquad (3)$$

where b is the concentration measured at the given measurement point, b_m is the mean concentration for a given period, angle K defines the direction of geostrophic wind which is necessary only when the sources around the measurement point are disposed unhomogeneously.Usually when measuring in the centre of a town it could be reasonably assumed that $\frac{b}{b_m}$ does not depend on the direction.

3. Statistical analysis of the air pollution

Fig.1 gives an example for a similar systematization of data. We have used the air pollution observations in the towns Krasnojarsk, Chita, Kursk, Leningrad, Svredlovsk, Novosibirsk, Krivoy Rog, Irkutsk published in [3],[4] and [5]. As a characteristic of air pollution we use the parameter $P = \frac{m}{n}$, where m is the number of observations with a concentration of 1.5 above the mean seasonal value for the period concerned. Since the mean P is approximately equal to 0.2 for the differents towns, cases with higher concentration of pollution are assumed $P > 0.2$ and are given on Fig.1 with black circlets. The cases $P < 0.2$ are given with white circlets and those $P \approx 0.2$ with asterisks. It is obvious that with great Rossby numbers and little S we have slight air pollution and vice versa.

4. Conclusion

The systematization of air pollution data by means of parameters (1) and (2) is very advantageous since those parameters are solely responsible for the diffusion process and could be obtained from the numerical weather forecast. With a sufficiently reliable statistic it enables us to predict air pollution. It is easy to make such a statistic when there are enough experimental air pollution data, since parameters (1) and (2) could be readily obtained from the synoptic maps or data of aerology for the corresponding past periods. The baroclinic effects influence mainly the high sources. In such cases two more external to PBL baroclinic parameters are added as shown in [2]. The statistic evaluation could be improved when some other parameters are included in (3), for example the parameter of inertia, giving the extent of pollution from the previous day. When designing new enterprises we should be able to determine the concentration patterns from them on the ground of synoptic data. A theoretical approach to the solution of this problem is studied in [6] and [7].

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EXPOSITIONSINDIKATOREN

INDICATORS OF EXPOSURE

INDICATEURS D'EXPOSITION

INDICATORI DI ESPOSIZIONE

INDICATOREN VAN EXPOSIE

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IL CONTENUTO DI PIOMBO NEI CAPELLI COME INDICE DI ESPOSIZIONE AL TOSSICO NELL'AMBIENTE

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RIASSUNTO

Data la crescente diffusione del piombo nell'ambiente vi è oggi la possibilità di intossicuzione saturnina non solo per gli operai che vengono a contatto con il tossico per motivi di lavoro, ma anche per le popolazioni civili, con gravi conseguenze per quanto riguarda i bambini.

Allo scopo di contribuire al controllo sia dello stato di esposizione sia dei casi iniziali di intossicuzione preclinica si è studiato se la ricerca del piombo nei capelli puo' costituire un indice di esposizione e di intossicazione.

In un gruppo di soggetti saturnini e in un gruppo di soggetti scelti a caso fra la popolazione si è determinato il tasso del piombo nel sangue, nelle urine e nei capelli. E' stata anche praticata la ricerca delle protoporfirine libere eritrocitarie, delle coproporfirine urinarie e dell'ALA urinaria.

Si è inoltre determinato il piombo nei capelli di gruppi di soggetti in quartieri diversi della città di Napoli.

E' stato trovato che vi è una differenza significativa fra la quantità di piombo nei capelli dei soggetti normali e dei soggetti saturnini. Inoltre il comportamento di questo parametro risulta molto simile a quello degli altri parametri studiati, e

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che vengono comunemente impiegati per la diagnosi biologica di saturnismo.

Non sono state trovate differenze significative nel contenuto di piombo nei capelli fra gli abitanti di quartieri diversi della città.

In conclusione, da questo studio risulta che la ricerca del piombo nei capelli puo' essere un mezzo molto utile per le indagini sul saturnismo e riguaranti grandi masse di popolazione.

ABSTRACT

In view of the increasing spread of lead in the environment, it is now possible for lead poisoning to affect not only workers who come into contact with the poison in the course of their work, but also the general population, with serious consequences for children.

To assist the investigation of the exposure situation and initial cases of pre-clinical poisoning, a study was made of whether the lead content of hair could be used as an index of exposure and poisoning.

The level of lead in the blood, urine and hair was determined in a group of subjects suffering from lead poisoning and in another group chosen at random from the population. The free protoporphyrins in red blood cells, the urinary coproporphyrins and the urinary ALA were also measured.

In addition, the lead content was measured in the hair of groups of subjects in different parts of the city of Naples.

It was found that there was a significant difference between the level of lead in the hair of normal subjects and in that of

subjects suffering from lead poisoning. This parameter was very similar to the other parameters investigated, which were those generally used in the biological diagnosis of lead poisoning.

No significant differences in the lead content of the hair were found between the inhabitants of different parts of the city.

To conclude, this study showed that determination of the lead content in hair might be a very useful method for studies of lead poisoning involving large sections of the population.

Introduzione

I metalli pesanti costituiscono una fonte importante e sempre più pericolosa di inquinamento ambientale. Per quanto riguarda il piombo è stato calcolato che negli ultimi 100 anni ne sono stati immessi nella biosfera oltre 100 milioni di tonnellate.

Ciò porta ad una crescente esposizione e ad un sempre più forte assorbimento del tossico da parte degli organismi viventi, per cui la possibilità di intossicazione non riguarda più solo coloro che vengono a contatto per motivi professionali, ma tutta la popolazione civile e in particolar modo i bambini, più sensibili al tossico specie per quanto riguarda il sistema nervoso.

Oltre le provvidenze per ridurre le fonti di inquinamento e limitare l'immissione nell'ambiente, è necessario non solo controllare il grado di esposizione delle popolazioni civili ma anche il tasso di assorbimento nei singoli individui e gli eventuali stati di intossicazione.

Sia per il gran numero di soggetti da esaminare, sia per le difficoltà pratiche del prelievo del sangue e della raccolta delle urine, specie nei bambini, sarebbe più agevole e più pratico un controllo eseguito attraverso la ricerca del piombo nei capelli.

Perchè ciò sia possibile è necessario accertare un effettivo e costante rapporto fra la quantità di piombo nell'ambiente, il grado di assorbimento, la piombemia, la piombiuria e agli altri parametri biologici impiegati per la diagnosi di saturnismo, con la quantità di piombo nei capelli.

Sinora pochi autori si sono occupati di questo argomento. Fra gli altri Kopito ha riportato 5 casi di bambini nei quali l'intossicazione saturnina fu sospettata per l'elevato tasso di piombo trovato nei capelli. Hammer ha trovato che la concentrazione di piombo ed altri metalli pesanti nei capelli di 5 città in USA riflette fedelmente i diversi livelli di esposizione ambientale.

Ricerche

Tenendo conto di queste premesse, abbiamo studiato il contenuto di piombo nel sangue, nelle urine e nei capelli di due gruppi costituiti da 42 soggetti normali e 41 soggetti saturnini. Sono stati anche ricercati i tassi delle protoporfirine libere eritrocitarie(PLE), delle coproporfirine urinarie(CPU), e dell'acido delta-aminolevulinico urinario(ALAU).

E' stato anche determinato il contenuto di piombo nei capelli, in gruppi diversi di vari quartieri della città di Napoli.

I risultati della prima indagine sono riportati nella tabella I. Si è trovato che i dati medi per ciascun parametro

TABELLA I

	Sangue Pb microg/100ml	Urine Pb microg/24 h	Capelli Pb microg/g peso secco	PLE microg/100ml globuli rossi	CPU microg/24 h	ALAU mg/24 h
Soggetti normali (42)	37±15	29±18	42±15	24±19	82±15	3,2±1,2
Soggetti saturnini(41)	118±24	132±27	114±23	201±38	172±20	7,4±2,3

TABELLA II

Contenuto di Pb nei capelli(microg/g peso secco)
in gruppi di vari quartieri della città di Napoli

Quartiere	N°soggetti	Pb
S.Lorenzo	11	41±7
Chiaia	15	38±2
S.Ferdinando	10	44±7
Ponticelli	12	37±8
Barra	11	44±5
Secondigliano	10	43±9
S.Giovanni	12	41±10

nel gruppo dei soggetti saturnini sono stati sempre e significativamente superiori ai dati corrispondenti nel gruppo disoggetti normali. Per quanto riguarda il contenuto di piombo nei capelli la media nei saturnini è risultata superiore di circa tre volte quella dei soggetti normali. Questo rapporto è quasi uguale a quello trovato per il piombo nel sangue e nelle urine (circa 4:1), per cui si può ritenere che la validità del rilievo è quasi la stessa per i tre paramentri.
Il tasso delle PLE nei saturnini è risultato molto elevato rispetto ai normali (8:1), mentre per quanto riguarda le CPU e l'ALAU il rapporto è circa uguale a quello trovato per i capelli.

I risultati della seconda indagine sono riportati nella tabella II, e non mostrano differenze significative fra i gruppi dei vari quartieri cittadini, per quanto riguarda il contenuto di piombo nei capelli.

Conclusioni

I risultati da noi ottenuti provano che la ricerca del piombo nei capelli può essere considerato un test valido dell' assorbimento organico del piombo. Inoltre la facilità del prelievo, la possibilità della conservazione e della ripetizione lo rendono adatto come primo esame su grandi masse di popolazione. Esso rende possibile di individuare facilmente i soggetti che possono essere coniderati normali e quelli che dovranno essere sottoposti ad ulteriori accertamenti per quanto riguarda l'assobimento di piombo e l'eventuale intossicazione. Inoltre la omogeneità dei dati di base, provata dal fatto che non sono state osservate differenze fra i gruppi nella popolazione di una grande città, rende più agevole la individuazione dei casi di aumentato assorbimento. Questo dato aumenta l'utilità dell'impiego della ricerca del piombo nei capelli come indagine di massa.

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APPLICATION OF LEAD MOBILIZATION FOR EXPOSURE EVALUATION

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ABSTRACT

Various parameters indicating lead exposure are followed. The investigation has been performed on following groups of persons showing various levels and duration of exposure:

I Group: workers exposed to high lead concentration for some months with acute clinical signs.
II Group: workers from the same place but without severe clinical symptoms.
III Group: workers with chronic lead poisoning.
IV Group: workers suspected of lead poisoning.
V Group: inhabitants living around a lead smelting plant.

For studied groups the following analyses are presented:

Hematologic determination in blood: Hb, erythrocytes, SRC, RTC. Toxicologic determination in urine: ALA, coproporphyrin, lead. Lead mobilization by 1 injection (for children ½ amp) of Ca Na_2*EDTA. Lead in urine was determined before injection and in 24 hours sample after.*

Analyzing obtained data it is quite obvious that mobilization of lead represents a very useful method, importance of

which depends on the level and duration of exposure. In acute and chronic poisoning all parameters are positive, including mobilization yield. On the other hand in the case of low but long exposure (inhabitants and workers in group IV) mobilization yield represent the most characteristic parameter pointing out the integral lead exposure.

For evaluation of the lead exposure many "exposure tests" are available. Generally, such tests are based on the direct determination of lead in biological samples (blood, urine) or on determination of the effects of toxic action of lead on porphyrin synthesis or on erythropoiesis. In environmental and occupational health, however, very often it is necessary to evaluate the integral exposure during the life. For such investigation all existing exposure tests are not useful. Recently some papers appeared suggesting evaluation of the lead body burden in the skeleton using "mobilization" by CaEDTA injection and determination of the quantity of excreted lead (mobilization yield) (1,2,3,4,5,6,7,8,9).

Here is presenting a study on various parameters, characteristic for lead exposure and mobilization yield in some groups of workers and a group of population with different level and duration of exposure. I group: 22 monters hospitilized in the Institute due to severe signs of poisoning (acute abdomen, lead colics, adinamy or digestive disturbances). They worked some months, exposed to high lead concentration 0,5-20mgr/m^3.

II Group: 13 monters from the same place with slight clinical signs reached the Institute 2 months after the end of work with lead exposure III Group: 31 workers exposed to lead 5-10 y. in battery factories treated into the Institute due to chronic lead poisoning. IV Group: 30 workers lead welders, who were examined as suspected on lead poisoning.

V Group: 124 inhabitants of a valley living 1-6 km from lead smelting plant emitting more than 200 t. of lead aerosols Concentration of lead in air was registered from 1,3-85 micrograms/m^3. In these persons ALA excretion was from 1,4-42 mgr/l varying in the course of years. In this group 20 males, 37 children and 67 females are included. In all persons mentioned analysis has been performed except ALA for groups I and II.

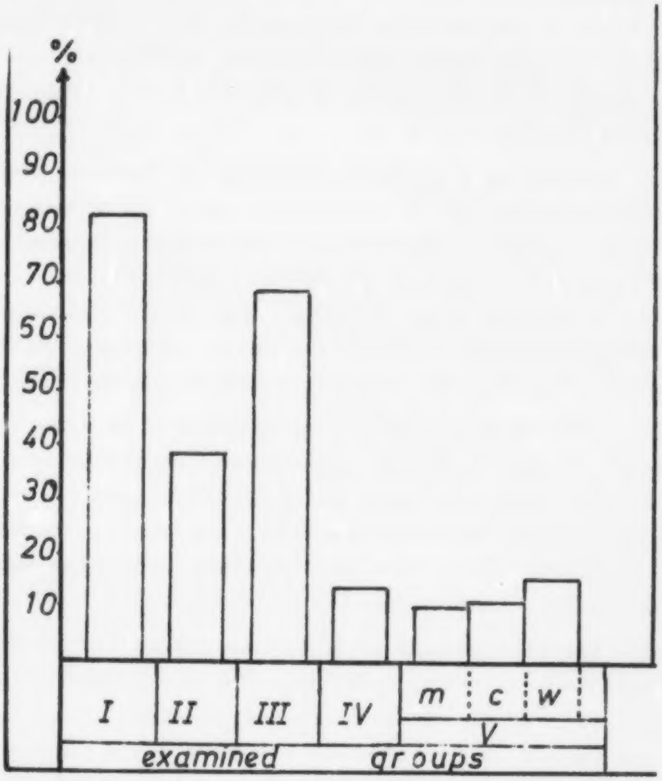
Results

Obtained results are presented in a series of graphs as percentage of cases with values out of normal limits. Percentage of cases with decreased Hb values under 80% (for women

and children 75% is presented on graph I. The lowest values of Hb were registered in group I (64% under 75% Hb).

GRAPH I

PERCENTAGE OF CASES WITH DECREASED
Hb VALUES UNDER 80%

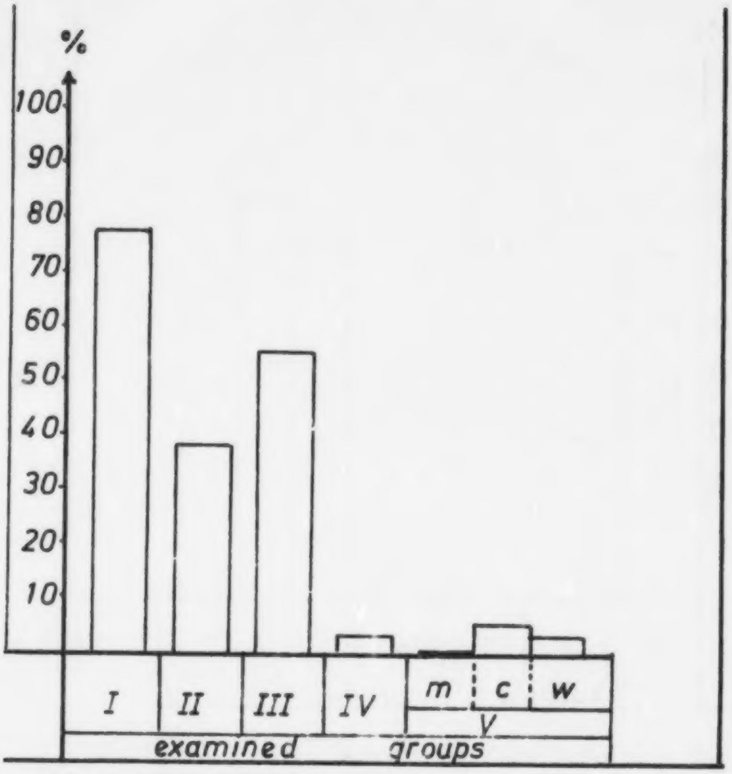


FOR WOMEN AND CHILDREN UNDER 75% Hb.

Percentage of persons with decreased number of Er under 3.900.000 (for women and children 3.600.000) is presented on graph II. In the group I also the lowest absolute numbers are evident, in 45% of examined less than 3 mil. In group IV and inhabitants decrease of Er is practically negligible.

GRAPH II

PERCENTAGE OF CASES WITH DECREASED NUMBER OF Er. UNDER 3.900.000

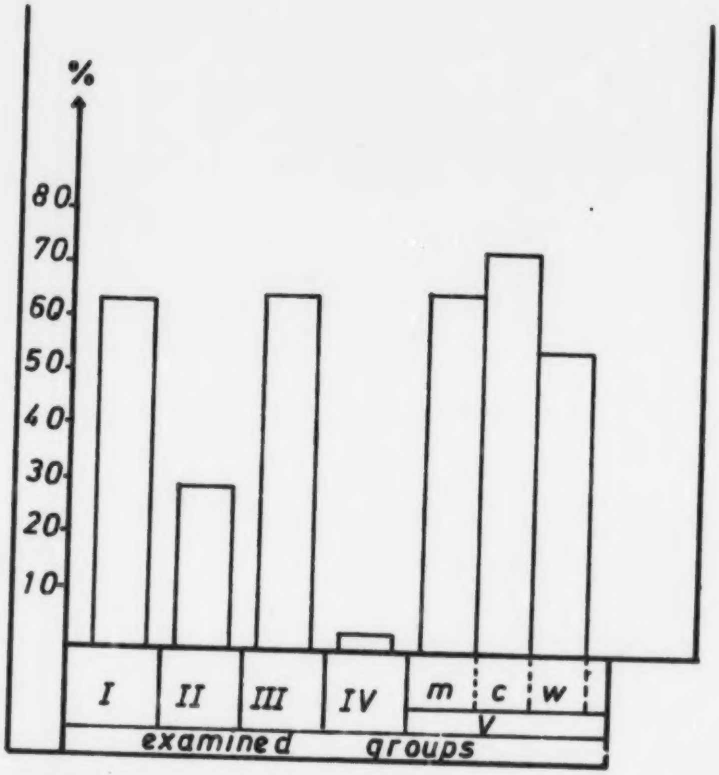


FOR WOMEN AND CHILDREN UNDER 3.500.000 Er.

On graph III the percentage of cases with the increased number of stipled red cells (SRC) over 300 on million Er. (for population over 100) is presented. Comparing the absolute number group I is showing 32% cases with over 2.000 RSC and group III only 19%. In population in 65% of males, 73% children and 55% of women we found increased number of RSC. To add that in 54% of children number of RSC was over 300.

GRAPH III

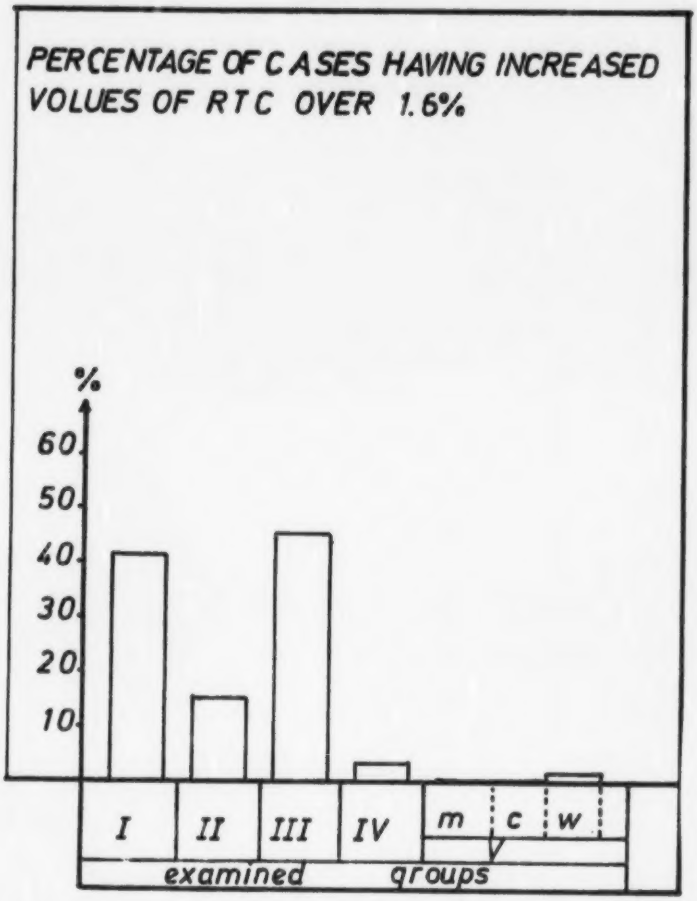
PERCENTAGE OF CASES HAVING INCREASED NUMBER OF SRC OVER 300 (MILLION Er.)



FOR POPULATION OVER 100 SRC MILLION Er.

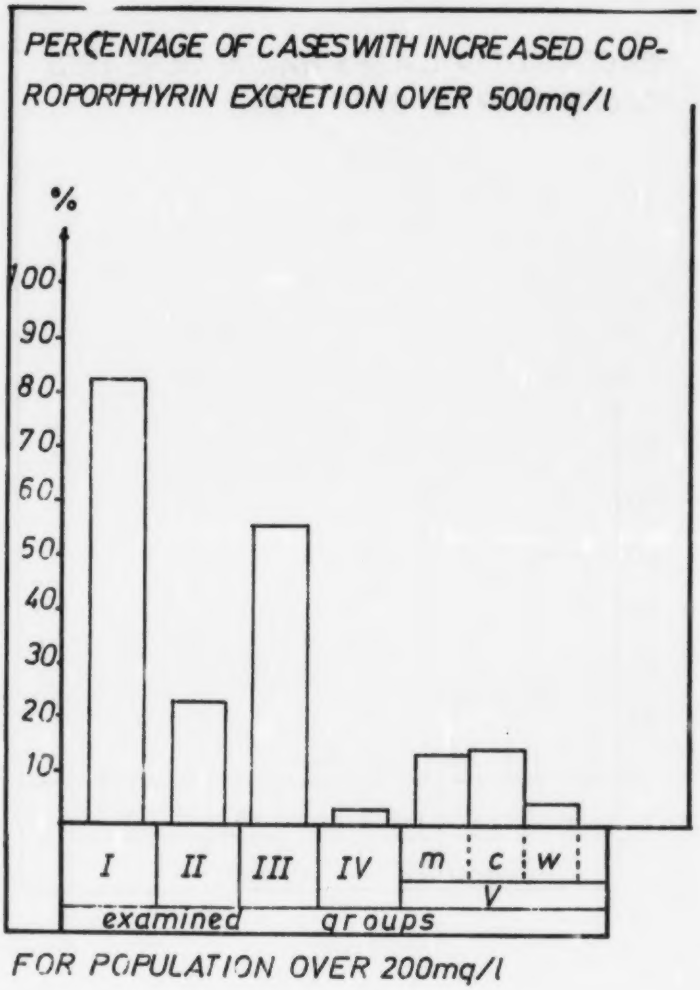
Next graph is presenting the percentage of cases with increased number of RTC over 1,6%. Group I and III are showing a moderate percentage of increased values. In other groups percentage of cases is negligible.

GRAPH IV



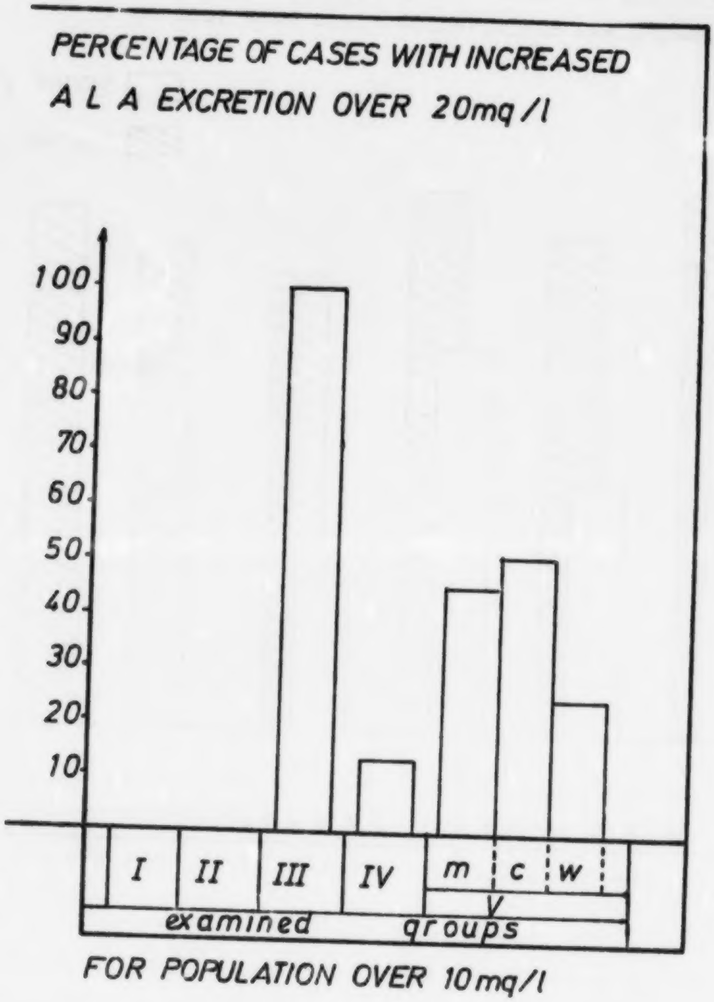
Graph V is presenting the percentage of persons with an increase of coproporphyrin excretion over 500 μg/l (for population over 200 μg/l). The highest values are found in group I; in 27% examined results are from 2000-5000 Mg/l.

GRAPH V



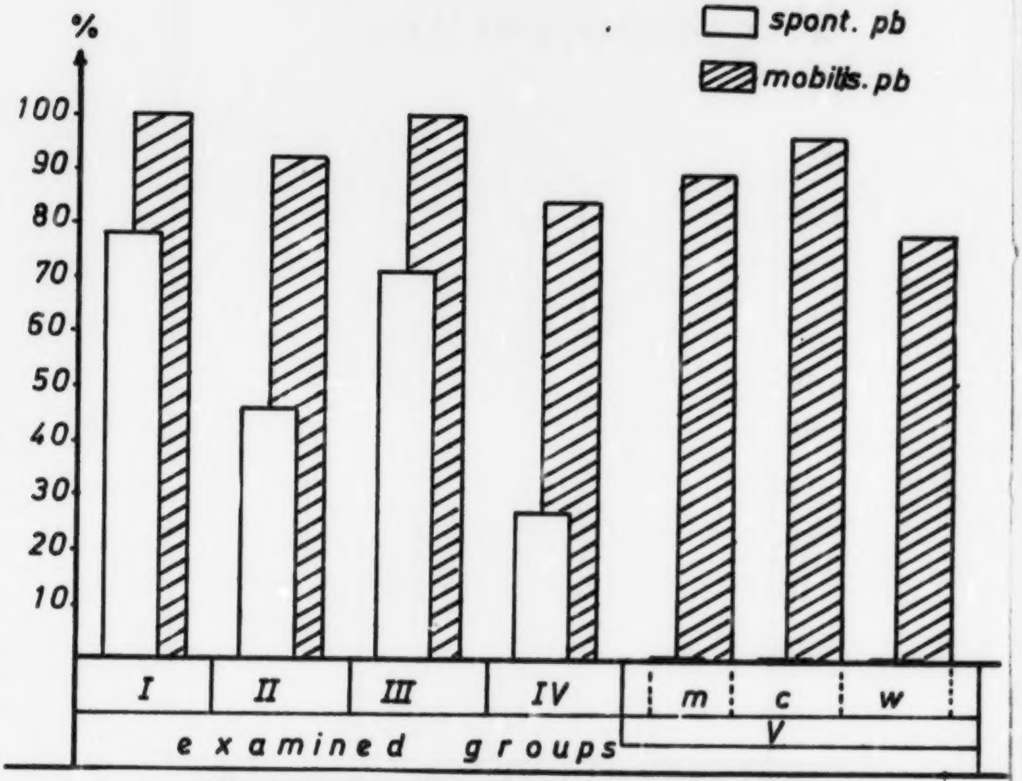
Graph VI is presenting percentage of cases with increased excretion of ALA over 20 mgr/l (for population 10 mgr/l). Results for group I and II are missing. In group III all examined had values from 20-100mgr.

GRAPH VI



Graph VII is presenting the percentage of cases with increased values over 120 μg/l of spontaneously excreted lead and the "mobilization yield". In group I excretion is increased in 78% of examined and 32% of them showed quantities over 300 μg/l. In group III the increase of excretion is registered in similar percent (71%) but only 3,2% of examined had the increase over 300 μg/l.

PERCENTAGE OF CASES WITH SPONTANEOUS EYCRETED LEAD OVER 120mg/1 AND MOBILISATION YIELD OVER 1000 mg/1



FOR POPULATION MOBILISATION YIELD OVER 500mg/1

In inhabitants 6% showed increased values of lead excretion. As normal mobilization yield is accepted for workers 1.000 μg/1 of lead and for population 500 μg/1. In all groups high percertage of cases with increased mobilization yield is evident, but a significant difference between groups exist in the quantity of mobilized lead. For example, in group I in 86% of cases mobilization yield is 2.000 - 4.000 μg/1, and in 9% even more than 4.000 μg/1. In group III values over 4.000 μg/1 are registered in 54% of examined. In population 86% of men, 96% of children and 78% of women excreted more than 500 µg/l of lead. The yield of 1.000 - 2.000 µg/l is registered in 41,3% men, 61% children and 18% women.

Discussion

Comparing parameters for each group some interesting observation could be made.

In group I with clinical signs of acute poisoning, all parameters are changed in high percentage of examined. Also the absolute value of each parameter is showing the greatest deflection from the normal value.

In group II with slight clinical symptoms the absolute values and percentage of deflection are smaller in relation to the first group. Here the spontaneous excretion of lead represents the most characteristic finding.

In group III (chronic lead poisoning) ALA excretion represents the most important findings; increase is established in all examined. In this group is lacking the parallel increase of coproporphyrin excretion. Comparing results obtained for group I and III it is possible to conclude that the percentage of cases with increase SRC and RTC in both groups are similar. In Hb, Er and coproporphyrin expressed difference in percentage is evident but it is not statistically significant.

In group IV (workers exposed to lower lead level) only decrease of Hb and increase of ALA represent characteristic parameters.

Exposure of population of lead is characterized by two parameters: SRC and ALA. ALA increase in population is more expressed than in workers of IV group. This could be explained probably by the fact that inhabitants of valley are exposed to lead 24 hours per day from birth.

We followed all parameters in inhabitants of valley for 5 years consecutively and found great variation each year, according to technologic and meteorologic conditions. But determination of mobilization yield gave us real apprehension of the size of the integral exposure from birth.

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BEZIEHUNGEN ZWISCHEN RAUMLUFTKONZENTRATION, BLUTSPIEGEL UND METABOLITENAUSSCHEIDUNG AROMATISCHER LÖSUNGSMITTEL

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KURZFASSUNG

Um den Beziehungen zwischen dem Gehalt von Toluol der Raumluft, seiner Konzentration im Blut und der Metabolitenausscheidung im Harn nachzugehen, wurden bei 94 Beschäftigten einer Druckerei Bestimmungen dieses Lösungsmittels im Blut und seines Metaboliten Hippursäure im Harn durchgeführt und den gleichzeitig erfolgten Raumluftmessungen gegenübergestellt. Bei einem Vergleich der gemessenen Toluolkonzentrationen in der Raumluft mit dem MAK-Wert für Toluol erschien arbeitsmedizinisch-toxikologisch die Belastung relativ gering. Trotzdem waren die mittleren Toluolkonzentrationen im Blut gegenüber den Werten einer Kontrollgruppe stark erhöht.

Es zeigt sich, dass eine Beurteilung der Gefährdung am Arbeitsplatz auf Grund von Raumluftmessungen mit erheblichen Unsicherheiten behaftet ist. Die Hippursäureausscheidung im Harn is ausserberuflichen Einflüssen unterworfen. Diese Einschränkungen gelten für eine Lösungsmittelbestimmung im Blut im wesentlichen nicht. Ein vorläufiger Grenzwert für einen arbeitsmedizinisch noch akzeptablen Bereich der Toluolkonzentration wird auf Grund der Untersuchungsergebnisse vorgelegt.

ABSTRACT

In order to investigate the relationships between the toluene content of air in an enclosed space, toluene concentration in the blood and excretion of toluene metabolites in the urine, the levels of this solvent in blood and of its metabolite hippuric acid in urine were determined in 94 employees of a printing works and compared with toluene levels in the air in the room measured at the same time. Compared with the MAC value for toluene, the atmospheric toluene concentration measured in the room seemed to indicate relatively slight exposure from an industrial medical and toxicological viewpoint. Despite this, the average toluene levels in the blood were very much higher than the figures for a control group.

It is clear that considerable uncertainty attaches to the assessment of health hazards at places of work from measurements of the room air concentrations. The excretion of hippuric acid in the urine is affected by non-occupational factors. In the main, these reservations do not apply to the determination of the solvent in the blood. On the basis of the experimental results, a provisional limit value is proposed for a range of toluene concentrations which is acceptable from the standpoint of industrial medicine.

Für eine Überwachung des Arbeitsplatzes ist es relativ einfach, die Konzentration aromatischer Lösungsmittel in der Raumluft zu bestimmen. Ein Vergleich dieser Raumluftanalysen mit den zugehörigen MAK-Werten ermöglicht in vielen Fällen eine Beurteilung des gesundheitlichen Risikos. Man muß sich jedoch darüber im klaren sein, daß diesem Vorgehen nicht mehr als eine orientierende Bedeutung zukommen kann. Individuelle Faktoren, etwa das Atemminutenvolumen, lassen sich nämlich häufig nicht gebührend berücksichtigen. Bestimmungen des jeweiligen Schadstoffes oder seiner Metaboliten im biologischen Material geben daher eine bessere Aussagemöglichkeit zur individuellen Belastung. Auf diese Weise können nämlich nicht nur inhalative Resorptionsquoten mit erfaßt werden, persönliche Faktoren oder spezielle Arbeitsplatzsituationen gehen ebenfalls integrierend in den Endwert ein.

Um den Beziehungen zwischen dem Gehalt von Toluol der Raumluft, seiner Konzentration im Blut und der Metabolitenausscheidung im Harn nachzugehen, wurden bei 94 Beschäftigten eines Tiefdruckbetriebes Bestimmungen dieses Lösungsmittels im Blut und seines Metaboliten Hippursäure im Harn durchgeführt und den gleichzeitig durchgeführten Raumluftmessungen gegenübergestellt. Die Toluolbestimmungen in Luft und Blut erfolgten gaschromatographisch nach einer anderenorts von uns beschriebenen Methode. Die Hippursäurebestimmungen erfolgten nach dem Verfahren von Lieberman.

Die Toluolkonzentrationen in der Raumluft schwankten je nach Arbeitsplatz zwischen 318 mg/m^3 und 935 mg/m^3. Die mittlere Toluolkonzentration im Blut von 68 Beschäftigten im Tiefdrucksaal lag bei 159,1 µg/100 ml (s = 107,0) und von 11 Tiefdruckern im Andruck bei 161,5 µg/100 ml (s = 118,4), während die mittlere Toluolkonzentration im Blut bei einem Kontrollkollektiv (n = 30) von Büroangestellten 5,3 µg/100 ml (s = 4,2) betrug. Für die Hippursäureausscheidung im Harn ergaben sich in der gleichen Reihenfolge 3,7 g/l (s = 2,2), 2,8 g/l (s = 1,8) und 0,82 g/l (s = 0,4).

Bei einem Vergleich der gemessenen Toluolkonzentrationen in der Raumluft mit dem MAK-Wert für Toluol erschien arbeitsmedizinisch-toxikologisch die Belastung relativ gering. Trotzdem waren die mittleren Toluolkonzentrationen im Blut gegenüber den Werten der Kontrollgruppe stark erhöht, die Unterschiede ließen sich varianzanalytisch mit einer Irrtumswahrscheinlichkeit von $p < 0,01$ sichern. Inwieweit hier temporäre Erhöhungen der Toluolkonzentration in der Raumluft (gemessene Spitzenwerte lagen bei 1872 mg/m^3) oder die Tatsache eine Rolle spielte, daß die Drucker ihre stark verschmutzten Hände regelmäßig in Toluol wuschen, mag dahingestellt bleiben. Unverkennbar ist jedoch, daß eine Abschätzung der Gefährdung am Arbeitsplatz allein auf Grund von Raumluftmessungen einen großen Unsicherheitsfaktor impliziert. Eine Beurteilung auf Grund der Hippursäureausscheidung im Harn ist jedoch auch nicht ohne Probleme. Es ist bekannt, daß die Hippursäure nicht nur ein Abbauprodukt von Toluol ist, sondern eine vermehrte Ausscheidung auch nach dem Genuß bestimmter Nahrungsmittel, etwa Backpflaumen oder Preiselbeeren, zu beobachten ist. Auch die zu Konservierungszwecken manchen Nahrungsmitteln zugesetzte Benzoesäure bewirkt eine erhöhte Hippursäureausscheidung. So kann es geschehen, daß die Hippursäureauscheidung zu Beginn einer Arbeitsschicht höher liegt als bei Schichtende, wie wir es in einem kürzlich durchgeführten weiteren Untersuchungsprogramm an Tiefdruckern in Einzelfällen sahen.

Die stark erhöhten Toluolkonzentrationen im Blut lassen zunächst nur die Aussage zu, daß es sich hierbei um eine vermehrte Belastung der Exponierten handelt. Um nun darüber hinaus auch konkrete Beurteilungskriterien über eine beginnende Vergiftung in die Hand zu bekommen, haben wir neben den quantitativen Toluolbestimmungen im Blut sämtliche für eine Beurteilung der Leberfunktion relevanten Parameter untersucht, wobei aus verständlichen Gründen bei einer derartigen epidemiologischen Studie von Leberbiopsien Abstand genommen werden mußte. Vorbehaltlich der noch nicht völlig abgeschlossenen Auswertung kann schon jetzt gesagt werden, daß es bis zu Toluolkonzentrationen im Blut von 400 µg/100 ml nicht zu klinisch oder labordiagnostisch objektivierbaren Leberschäden kommt. Man wird diesen Wert zunächst als einen vorläufigen Grenzwert ansehen können, der den arbeitsmedizinisch akzeptablen Bereich charakterisiert. Darüber hinaus hoffen wir, durch eine Verknüpfung der Toluolkonzentration im Blut mit der zugehörigen Hippursäureausscheidung im Harn zu noch differenzierteren Aussagen zu kommen. Dazu sind jedoch noch weiterführende Untersuchungen und statistische Analysen notwendig.

1847.

GEWEBSMESSUNGEN

TISSUE MEASUREMENTS

MESURES RELATIVES AUX TISSUS BIOLOGIQUES

MISURE NEI TESSUTI BIOLOGICI

METING VAN BIOLOGISCH WEEFSEL

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HOW USEFUL ARE THE BULK OF ENVIRONMENTAL DATA?

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ABSTRACT

It is crucial in the setting of environmental or health standards that a reliable data bank be available. Unfortunately a review of the literature on most pollutants reveals that there is frequently no way to judge the validity of the numbers which are given. Reasons are poor documentation and control of sampling, sample preparation and the subsequent analysis.

The inadequacies of data have been demonstrated frequently but never more clearly than in the case of mercury pollution problems around the world. Mercury analyses have been done routinely for most of this century. Much of the work was undoubtedly carried out using so-called "standard methods", commonly available from health and pollution control organizations. However, it was only subsequent to the 1953 Minamata incident that the true chaotic nature of mercury data was revealed. In fact the literature shows that as recently as 1971 little agreement could be found even on the choice of the analytical method.

In this presentation evidence of deficiencies in other health related data banks e.g. blood lead values, will also be discussed. Suggestions will be made regarding a more rational approach in the future.

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1. INTRODUCTION

Reviewing the literature for environmental chemical data reveals that there is frequently no way to judge validity of the numbers. Reasons are poor documentation and control of some, most, or all aspects of the analytical process including sampling, chemical analysis procedures, and data dissemination. These inadequacies cause serious problems when government standards for environmental quality have to be decided upon and enforced.

2. DOES USE OF A "STANDARD METHOD" GUARANTEE USEFUL DATA?

It is commonly believed that use of a "Standard Method" (one published by a number of health and pollution control organizations) is sufficient to validate data produced. In published environmental studies it is common place to find that the description of analytical methods and assessment of the validity of the results consists only of a reference to the use of a "standard method".

A number of authors (e.g. ref.3,4) have provided data to show that the use of standard methods does not necessarily result in accurate results. In addition performance of a laboratory must be continually be evaluated through use of interlaboratory control samples, "standards" and participation in round robin studies.

3. MERCURY - A GOOD EXAMPLE OF INADEQUACIES IN DATA

What happened when high levels of mercury were found in fish is a good example of the problems to be faced in setting and enforcing environmental standards. When the dangers of mercury were realized, a limit was put on the amount allowed in fish flesh offered for sale in Canada and the United States. Because of the almost complete lack of valid data, however, the selection of an 0.5-ppm level, was, at best, an educated guess. Fortunately, as the vast quantities of useful data now accumulating are evaluated, this arbitrary choice is being justified.

In establishing permissible levels for a substance such as mercury in fish, many questions must be asked. What are the normal background levels for mercury in various fish species? What levels of mercury can be safely tolerated by the human population in question? Is there analytical data of suitable validity to allow sensible answers to either of these questions? When officials were faced with the task of establishing the permissible mercury content of fish, the answer to this last question was an emphatic no !

The inadequacy of mercury data is well documented in the literature. The Niigata report (2) in 1967 shows variations between neutron activation (NA) and dithazone mercury values, for the same sample, of up to 100%. In 1970, 13 laboratories analyzed a mercury spiked, flour sample by the same method (NA) (5). A mean value of 4.6 ppm was obtained with a range of values for 10 of the 13 laboratories of 1.4 ppm. The other laboratories were outside this range, one giving a value deviating from the mean by 50 times! In 1971 two homogenized fish samples were analyzed by (NA) and flameless atomic absorption spectroscopy (FAAS) (6) Results showed that although the mean values for each technique were close, 1.37 ppm (FAAS), 1.36 ppm (NA) for sample 1 and 0.11 ppm (FAAS), 0.10 ppm (NA) for sample 2 there was a wide range of values submitted by the laboratories, 0.9 to 1.8 and 0.03 to 0.21 respectively.

In light of the variability of this data one might ask how it is possible to enforce a limit of 0.5 ppm mercury for fish flesh. A recent evaluation of the performance of laboratories engaged in mercury analysis has shown that with a careful selection of good laboratories, data in good agreement for standard samples can be obtained (1). Gelatin samples spiked with known amounts of mercury were sent to 18 laboratories. Results collected from all these laboratories on a sample spiked with 2 ppm mercury showed a mean of 2.02 ppm and a maximum range of from 1.88 to 2.18 ppm - a variation of 15% at this level of concentration. This is a vast improvement over performances at earlier times recorded above.

In spite of this, it could still be asked whether the same laboratories would perform with the same reliability after doing their own sampling and then analysing a natural sample such as a fish. Fortunately samples more like those chemists actually test, such as leaves, liver, and fish flesh, are now being prepared and tested as standards for mercury analysis. How laboratories will perform on these samples is yet to be seen. Because of this, it still remains a question in this writer's mind how closely the 0.5 ppm limit set for mercury in fish flesh can be reasonably enforced.

4. WHAT ABOUT THE FUTURE?

Few environmental pollutants have been the subject of such an intensive appraisal of data validity as mercury. Fortunately, in this case the arbitrarily chosen limit of 0.5 ppm seems to be standing the bombardment of valid data. One must, however, worry about sudden needs to set limits in the future for other substances in the environment. Will we have the same luck as we did with mercury? Will skilled analytical chemists help us approach the problem in a more rational way? Or will inadequacies in chemical data force us to guess about questions vital to health?

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AUSWIRKUNGEN DER BLEI-UMWELTKONTAMINATION AUF LEBENSMITTEL VON SCHLACHTTIEREN: EIN BEITRAG ZUR PROBENAHME UND BEURTEILUNG

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KURZFASSUNG

Von 139 Rindern aus einem vorwiegend landwirtschaftlich strukturierten Gebiet des schwäbisch-bayerischen Voralpenlandes und 22 Tieren aus stärker bleiexponierten Arealen der BRD wurden in Fleisch, Leber und Niere von jedem Tier nach nasser Mineralisation mit H_2O_2/Fe^{++} *der Pb-Gehalt flammenlos atomabsorptionsspektrometrisch bestimmt.*

Mit nur 2 Ausnahmen enthielten die Nieren der Tiere aus dem Voralpenland stets die höchsten Pb-Gehalte, gefolgt von Leber und Fleisch. In den Nieren variierten die Pb-Konzentrationen zwischen 0,10 und 0,80 ppm, in den Lebern zwischen 0,05 und 0,40 ppm; im Fleisch lagen sie fast immer unter 0,05 ppm. Die Variationskoeffizienten betrugen bei Lebern 54,2%, bei Nieren 39,0%. Sie dürfen primär individuell verursacht sein. Eine Abhängigkeit der Pb-Konzentration in Nieren und Leber von Alter, Geschlecht und Jahreszeit war daher statistisch nicht abzusichern. Dagegen bestand zwischen den Nieren- und Leber-Pb-Gehalten der Rinder ein hochsignifikanter Zusammenhang.

Das Fleisch stärker bleiexponierter Rinder enthielt selbst dann, wenn die Tiere mit Symptomen einer Pb-Intoxikation notgeschlachtet werden mussten, kaum erhöhte Pb-Gehalte, Nieren und Lebern jedoch ein mehr als 100-faches der Konzentrationen wie in Nieren und Lebern der Rinder aus dem Voralpenraum. Eine eindeutige Abhängigkeit von der Expositionsintensität konnte dabei jedoch nicht festgestellt werden.

Fleisch kann als ein Pb-armes, Nieren als ein Pb-reiches Lebensmittel gelten, Lebern als durchschnittlich Pb-haltig. Der Beitrag von Fleisch, Lebern und Nieren zum Gesamt-Pb-Gehalt der Nahrung ist gering.

ABSTRACT

The lead content of the flesh, liver and kidneys of each of 139 heads of cattle from a predominantly agricultural subalpine area of Swabia and Bavaria, and of 22 animals from areas of the German Federal Republic which are more severely exposed to lead, was determined by atom absorption spectrometry under flame-free conditions after wet mineralization with H_2O_2 / Fe^{++}.

With only 2 exceptions, the kidneys of animals from the subalpine area always had the highest lead contents, followed by the liver and flesh. In the kidneys the lead concentrations were in the range 0.10 - 0.80 ppm, in the livers they were 0.05 - 0.40 ppm, and in the flesh they were almost always below 0.05 ppm. The coefficients of variation were 54.2% in livers and 39.0% in kidneys. They may depend primarily on individuals. Hence, a dependence of lead concentration in the kidneys and liver on age, sex, and season could not be established statistically. On the other hand, there was a highly significant correlation between the lead contents of the kidneys and livers of the cattle. The flesh of cattle more heavily exposed to lead showed hardly any increase of lead content even when the animals

had to be emergency slaughtered with symptoms of lead poisoning, but the kidneys and livers showed concentrations more than 100 times as high as those in the kidneys and livers of the cattle from the subalpine region. However, it was not possible to establish a definite dependence on intensity of exposure.

Flesh can be considered to be a food with a low lead content, kidneys as one with a high lead content, and liver as one with an average lead content. The contribution of flesh, liver and kidneys to the total lead content of the diet is small.

1. Einleitung

Über die Auswirkungen der Aufnahme geringer Mengen Pb für längere Zeit auf den menschlichen Organismus ist relativ wenig bekannt. Unklarheit besteht vor allem über seine Langzeittoxizität. Pb reichert sich in den Knochen, aber auch in Leber und Nieren des Körpers an und übt offenbar schon in schwachen Konzentrationen bestimmte biologische Wirkungen aus.

Die Hauptzufuhrquelle stellt dabei, bestimmte Extremsituationen ausgenommen (Emissionen von Pb-Hütten, Pb-verarbeitender Industrie, Großstadt), die Nahrung dar. Mit ihr werden dem menschlichen Körper mehr als die Hälfte seiner Gesamt-Pb-Aufnahme zugeführt (10, 44, 47). Die WHO veranschlagt diesen Anteil auf 57 - 66 % (47).

Allein schon deshalb beansprucht Pb als potentieller Rückstandsbildner in Lebensmitteln lebensmittelhygienische Beachtung. Tierischen Lebensmitteln kommt dabei besondere Bedeutung zu, da Pb in ihnen überwiegend organisch gebunden vorliegt. Die leichter löslichen organischen Pb-Verbindungen sind aber einer Resorption im Verdauungstrakt leichter zugänglich als die im allgemeinen weniger gut löslichen anorganischen.

Wenn auch bis jetzt beim Menschen noch keine augenscheinlichen Pb-Langzeitintoxikationssymptome beobachtet werden konnten, hält man aus Unkenntnis der Pb-Langzeitintoxikationswirkung eine weitere Zunahme der Pb-Belastung in Umwelt und Bevölkerung nicht allein aus Gründen der Vorsicht für kaum mehr vertretbar.

Im Interesse des Konsumentenschutzes haben deshalb bereits verschiedene Staaten für Lebensmittel zulässige Pb-Höchstwerte festgelegt, andere, unter ihnen die BRD, erwägen gegenwärtig deren Festsetzung.

Dies gab Veranlassung, ab Frühjahr 1972 Fleisch- und Organproben von Schlachtrindern auf ihren Pb-Gehalt zu untersuchen.

Diese Untersuchungen dürften außerdem Hinweise auf das Verteilungsmuster des Pb im Rinderorganismus und über den An-

Tabelle 1: Pb-Konzentrationen (ppm/Fg) in Fleisch, Leber und Nieren von Schlachtrindern

	Muskulatur	n	Leber	n	Nieren	n	Land	Unters.-Jahr	Literatur
			0,10-0,25	4	0,10-1,00	4	D	1934	8
	0,16						D	1963	5
	0,29-1,65	8					D	1968	28
	<0,1	10	<0,1	10	<0,1	10	D	1970/71	13
	0,092 (0,03-0,35)	127	0,1-1,4		0,26-1,7		D	1972/73	15
JgBulle/ Färse	0,96	30					D	1972/73	16
	0,1						CH	1960	20
			0,3-1,5		0,3-1,5		GB	1951	1,2,3
	0,01-0,50						GB	1971/72	45
			0,4-1,7	6			GB	1969	34
	<1,0		<1,0				I	1966	22
Frühling	<0,1		0,17-0,54	25			S	1969	33
Herbst	<0,1		0,20-0,92	25			S	1969	33
	0,015	5	0,085	5			SF	1969	23
	0,07-0,2						USA	1961	40
			0,3-0,5				USA	1966	32
	0,003-0,63							1961	9

teil des Rindfleisches am Pb-Gehalt der Gesamtnahrung, bei Fleischerzeugnissen auchRückschlüsse auf eine bei der Herstellung und Verpackung erfolgte Kontamination geben. Möglichkeiten dazu bestehen beim Kontakt mit Pb-haltigen Maschinenteilen oder dem Zusatz von Gewürzen und Fremdstoffen.

Einen Überblick über bisher in Fleisch, Lebern und Nieren von Rindern ermittelte Pb-Konzentrationen gibt Tabelle 1. Aus den Daten ist jedoch mit Ausnahme der Ergebnisse von HECHT, MIRNA und SCHRAML (17) sowie GRAHWIT (13) nicht ersichtlich, welche Fleischstücke untersucht wurden und ob die analysierten Fleisch-, Leber- und Nierenproben jeweils von einem oder von verschiedenen Schlachtkörpern entnommen worden sind. Außerdem fehlt es i.d.R. auch an Hinweisen zur Probenahme, insbesondere an Angaben über Alter, Geschlecht, Rasse, Haltung und Fütterung.

2. Untersuchungen

2.1.: Untersuchungsmaterial

Von 77 am 12.5., 5.7., 26.7. und 13.12.1972 sowie 62 am 14. 3., 19.6., 18.7. und 25.9.1973 geschlachteten Rindern unterschiedlichen Alters (0,8 - 15 Jahre), Geschlechts und verschiedener Rasse wurden pro Tier jeweils 100 - 200 g schwere Proben aus den Mm. adductores, dem Lòbus caudatus der Leber und dem apikalen Pol der rechten Niere schlachtfrisch entnommen und bis zur Analyse tiefgekühlt aufbewahrt.

Fleisch war für die Untersuchungen wegen seiner Bedeutung in der menschlichen Ernährung ausgewählt worden, Leber und Nieren als Target- und vermutliche Speicherorgane des Pb im tierischen Organismus.

Für die Entnahme der Fleischproben empfahlen sich bei der großen Konstanz ihrer grobgeweblichen Zusammensetzung die Mm. adductores (26).

Die sehr inhomogene Verteilung des Pb in Lebern (25; 26) und Nieren (25) veranlaßte, die Proben immer gleichen Stellen dieser Organe zu entnehmen, um die Reproduzierbarkeit der Ergebnisse zu sichern.

Die Rinder stammten aus einem vorwiegend landwirtschaftlich strukturierten Gebiet des schwäbisch-bayerischen Voralpenlandes mit Weidehaltung im Sommerhalbjahr. Das Probeneinzugsgebiet liegt zwischen den Orten Augsburg - Memmingen - Ettal - Weilheim und Fürstenfeldbruck.

In diesem Areal schwanken die langjährigen Niederschlagsmittel zwischen 700 mm im Raume Augsburg und 1200 mm Niederschlag im Ammergebirge (Ettal). Dieses Gebiet war ausgewählt worden, weil es als repräsentativ für andere, ähnlich strukturierte landwirtschaftliche Gebiete Mitteleuropas gelten kann. Verschiedentlich konnten dabei wiederholt Proben von Tieren aus gleichen Ortschaften bzw. gleichen Betrieben entnommen werden.

Auswahl der Tiere und Schlachttermine sollten die Prüfung eines eventuellen Einflusses von Alter, Geschlecht, Herkunft, Jahreszeit und Fütterung auf die Pb-Konzentrationen in Fleisch, Leber und Nieren ermöglichen.

Zum Vergleich waren noch Proben von Rindern aus verschiedenen stärker Pb-exponierten Gebieten der BRD untersucht worden. Sie stammten von

a) klinisch gesunden Rindern aus Betrieben in unmittelbarer Autobahnnähe und aus der Wesermarsch, wo im Frühjahr 1972 mehr als 60 Rinder wegen einer schadhaften Filteranlage des Preussag-Hüttenbetriebes verendet waren und

b) von mit Verdacht auf Pb-Vergiftung notgeschlachteten Tieren aus der Wesermarsch, aus 2 weiteren Gebieten der BRD, wo immer wieder Rinder an den Symptomen einer Pb-Intoxikation sterben und

c) von Tieren, die nach Aufnahme von Mennige notgeschlachtet werden mußten.

2.2 : Methodik

Die Bestimmung des Pb in Fleisch-, Leber- und Nierenproben erfolgt flammenlos atomabsorptionsspektrometrisch im Graphitrohr (Perkin-Elmer HGA 70 und 290 G). Das Untersuchungsmaterial, bei Fleisch, Leber und Nieren je 100 g, wird zu diesem Zweck mit HNO_3 suprapur und H_2O_2 (DAB 7) naß verascht, vorhandenes Fett abfiltriert, das Pb aus einem Aliquot der Lösung durch Fällung mit NH_4OH angereichert, abzentrifugiert und zur Injektion in das Graphitrohr in 20 ml salpetersaurer Lösung aufgenommen. Die Ausbeuten werden mittels trägerfreiem radioaktiven ^{212}Pb kontrolliert und schwanken zwischen

Tabelle 2: Pb-Konzentrationen (ppm/Fg) in Fleisch, Leber und Nieren 1972 geschlachteter Rinder (n = 77)

Datum	n	Alter±s(a)	Leber±s	V (%)	r*	Niere±s	V (%)	r*	Pb-Konz. Nieren/Leber	Fleisch
12.4.	11	4,5±3,2 (1,0-9,0)*	0,21±0,09 (0,08-0,39)	42,8	0,39	0,43±0,23 (0,18-0,80)	53,5	-0,26	2,5 (0,8-6,2)	0,09 (<0,05-0,24)
5.7.	17	4,3±3,1 (0,8-10,0)	0,13±0,06 (0,05-0,2)	46,2	0,00	0,32±0,14 (0,10-0,51)	43,8	0,13	2,5 (1,0-4,5)	<0,05
26.7.	22	5,3±3,0 (2,6-11,0)	0,15±0,05 (0,06-0,23)	33,3	0,20	0,35±0,12 (0,14-0,57)	34,3	0,09	2,5 (1,3-4,5)	<0,05
27.9.	15	7,4±3,5 (2,0-15,0)	0,16±0,05 (0,06-0,23)	31,3	-0,14	0,37±0,15 (0,16-0,80)	42,9	-0,05	2,4 (1,7-6,3)	<0,05
13.12.	12	6,4±1,2 (5,0-8,5)	0,17±0,06 (0,09-0,28)	39,2	-0,17	0,27-0,05 (0,20-0,35)	18,5	-0,11	1,7 (0,8-2,5)	<0,05
1972	77	5,3 (0,8-15,0)	0,16±0,07 (0,05-0,39)	43,8		0,34±0,15 (0,10-0,80)	44,1		2,4 (0,8-6,3)	<0,05

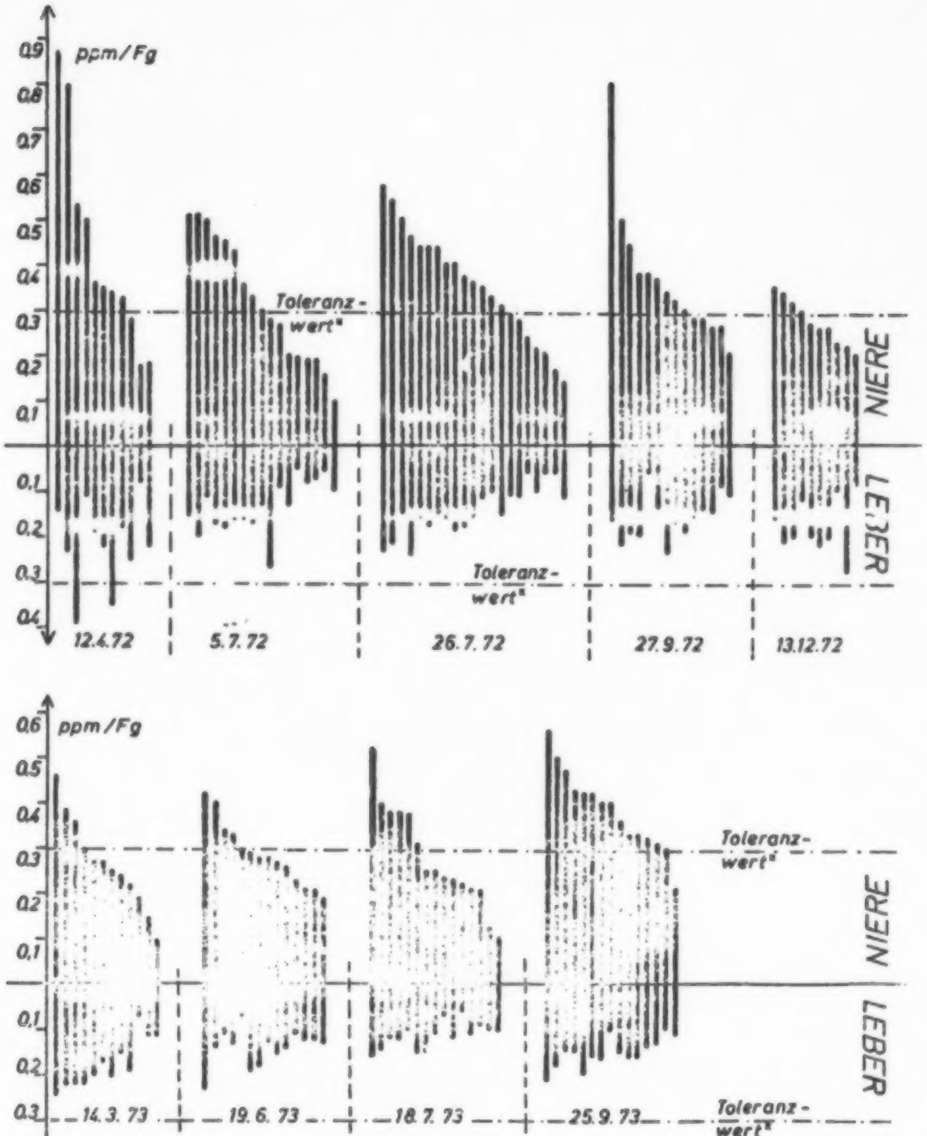
* = Schwankungsbreite der Einzelwerte

Tabelle 3: Bleikonzentrationen (ppm/Fg) in Fleisch, Leber und Nieren 1973 geschlachteter Rinder (n = 62)

Datum	n	Alter±s(a)	Leber±s	V (%)	r*	Niere±s	V (%)	r*	Pb-Konz. Nieren/Leber	Fleisch
14.3.	12	5,3±1,9 (2,0-9,0)	0,17±0,06 (0,10-0,24)	±39,2	0,07	0,27±0,10 (0,10-0,22)	±37,0	0,18	1,6 (1,2-2,7)	<0,05
19.6.	17	4,0±2,3 (1,5-10,0)	0,13±0,04 (0,07-0,23)	±30,8	0,07	0,39±0,46 (0,18-2,75)	±117,9	0,13	2,2 (1,5-4,3)	<0,05
18.7.	17	5,5±2,7 (1,5-11,0)	0,12±0,03 (0,06-0,40)	±25,0	0,27	0,28±0,11 (0,14-0,52)	±39,3	0,28	2,5 (1,2-3,8)	<0,05
25.9.	16	4,8±2,4 (1,5-10,0)	0,15±0,03 (0,10-0,21)	±20,0	0,13	0,38±0,09 (0,21-0,56)	±23,7	0,10	2,7 (2,1-4,0)	<0,05
1973:	62	4,9 (1,5-11,0)	0,14±0,04 (0,06-0,40)	±28,6		0,30±0,10 (0,10-2,75)	±33,3		2,7 (1,2-4,3)	<0,05

r* = Korrelationskoeffizient

V = Variationskoeffizient



*s. Tabelle 6

ABBILDUNG 1: Bleikonzentrationen in Nieren und Lebern von Schlachtrindern aus dem oberbayerisch-schwäbischen Voralpengebiet

85 - 95 %. Die Nachweisgrenze liegt für 100 g Einwaage bei 20 ppb, der Gesamtfehler der Pb-Bestimmung bei <10 %.

3. Ergebnisse

Die Durchschnittswerte, Standardabweichungen, Streubereiche und Variationskoeffizienten der Pb-Konzentrationen in Lebern und Nieren gibt für die 1972 geschlachteten Rinderkollektive Tabelle 2 und für das Jahr 1973 Tabelle 3 wieder. Beide Tabellen enthalten noch jeweils das Jahresdurchschnittsmittel, dessen Standardabweichung sowie Variationskoeffizienten und geben Auskunft über den Umfang der Probenkollektive, das Alter der Tiere, den Korrelationskoeffizienten zwischen der Pb-Konzentration von Leber und Niere und dem Alter der Tiere sowie den Quotienten der Pb-Konzentrationen von Nieren und Lebern.

Die Einzelwerte der Leber- und Nierenkonzentrationen sind für alle untersuchten Rinder aus Abbildung 1 ersichtlich. Ihre Anordnung erfolgte in Schlachtkollektiven nach fallender Nieren- Pb-Konzentration. Gleichzeitig veranschaulicht die Tabelle auch die inter- und intraindividuellen Unterschiede im Pb-Gehalt beider Organe und deren eventuelle jahreszeitliche Abhängigkeit.

Tabelle 5 faßt außerdem noch die Nieren- und Lebereinzelwerte zu Konzentrationsklassen zusammen, wobei ein Klassenintervall jeweils 0,1 ppm beträgt.

Tabelle 4 informiert über die Pb-Konzentration in Fleisch, Leber und Nieren der stärker Pb-exponierten Rinder. Die Daten sind durch entsprechende Angaben aus der Literatur ergänzt. Die Tabelle weist auch für Rinder in Leber und Nieren vermutlich toxische, offensichtlich toxische und tödliche Pb-Konzentrationen aus.

In Tabelle 6 sind verschiedene zur Zeit diskutierte, empfohlene oder für Fleisch und Organe bereits gültige Pb-Toleranzwerte zusammengestellt.

4. Besprechung und Diskussion der Ergebnisse

Bei 137 von 139 aus dem bayerischen Voralpenraum untersuchten Rindern enthielten die Nieren stets die höchsten Pb-Konzentrationen. Es folgen Leber und Fleisch. Lediglich in 2 Fällen wiesen die Lebern die höheren Konzentrationen auf. Ein

Tabelle 4: Pb-Gehalte (ppm/Fg) in Fleisch, Lebern und Nieren stärker Pb-exponierter Rinder

	Alter a	Fleisch	Leber	Niere	n	Jahr a	Literatur
Klin.ges.Rinder							
1. Großstadtnähe		0,42±0,71	0,23±0,48	0,42±0,59	20	1971/72	13
2. Autobahnnähe (massiv Expos.)	3,5	0,08	0,66	1,44		1972	
3. Wesermarsch	1-6	0,02-0,03	0,23-0,85	0,64-1,91	7	1972	
Notgeschl.Rinder (Verd.Pb-Vergiftg.)							
1. Wesermarsch	5,5	0,08	2,89	2,60		1972	
2. Wesermarsch		0,15.0,98	3,87-11,73		8	1972	15/16/17
3. Anderer Herkunft	2-6	0,11-0,38	3,80-12,20	4,9-22,8	7	1972/73	
4. Anderer Herkunft		< 0,1	18,0-22,8	23,2-62,8	5	1971/72	13
Aufnahme v.Mennige	3-6	0,04;0,07 0,09;0,18	5,7;20,2 3,1;4,4	14,0;59,0 7,6;5,9	4	1971	24
Vermutl.tox.Konz.			2- 20	10- 25	Lit	L.14;35;38;39; N.1;2;6;14;21;27;35	
Offens.tox.Konz.			4- 20	10- 50		L.14;30;35;42;43; N.6;11;14;21;27;30;35;43;	
tödliche Konz.			> 20	> 25		L.1;2;31; N.1;31;42;43;	

Tabelle 5: Zusammenstellung der Einzelwerte (Leber, Nieren) nach Konzentrationsklassen (ppm Pb/Fg)

	Lebern		Nieren	
Klassen	Probenzahl	Anteil in %	Probenzahl	Anteil in %
≤0,1	0	0	24	18,6
0,1-0,2	14	10,9	79	61,2
0,2-0,3	44	34,1	24	18,7
0,3-0,4	36	27,9	2	1,5
0,4-0,5	21	16,3		
0,5-0,6	11	8,5		
0,6-0,7	0	0		
0,7-0,8	1	0,8		
0,8-0,9	2	1,5		

Tabelle 6: Verschiedene für Fleisch und Organe von Schlachttieren diskutierte und vorgeschlagene zulässige Pb-Höchstwerte (ppm/g Fg)

WHO/FAO Expert Committee: Vorläufiger wöchentlicher Toleranzwert für Lebensmittel: 3,0 mg

Land	Fleisch	Innereien	Fleischerzeugnisse	
BRD:				
VO-Entwurf	0,05	0,3	0,1	46
Empfehlung	0,2	0,5*		
		2,0**		12

*ohne Nieren, **Leber

Grund hierfür vermag nicht genannt zu werden. Möglicherweise hatten beide Tiere kurz vor der Schlachtung mehr Pb aufgenommen als die anderen Rinder.

Mit Ausnahme des am 12.4.72 geschlachteten Tierkollektivs lagen die Pb-Konzentrationen im Fleisch stets unter 0,05 ppm/Fg. Die Tiere dieses Kollektivs waren vermutlich mit Futter, insbesondere Heu und Grummet aus dem Jahr 1971 ernährt worden. 1971 fielen in Mitteleuropa extrem wenig Niederschläge. Trockenes Wetter aber begünstigt im Grünfutter hohe Pb-Kontaminationen.

Lebern enthielten durchschnittlich 0,16 ppm, Nieren 0,33 ppm Pb/Fg. Die Minimalwerte betrugen bei Lebern 0,09 ppm und bei Nieren 0,10 ppm, die Maximalwerte 0,40 ppm bzw. 2,75 ppm. Die Niere mit dem Pb-Gehalt von 2,75 ppm stammt möglicherweise von einem Rind, das entweder längere Zeit bleireiches Futter aufgenommen oder früher einmal Zutritt zu stark Pb-haltigen Gegenständen besessen hatte.

Die Nieren enthielten, wie die Quotienten aus der Nieren- und Leber-Konzentration ausweisen mehr als doppelt so viel Pb wie die Lebern (Minimalwerte: 0,8, Maximalwerte: 6,3).

Besonders fällt in Lebern und Nieren die große Streuung der Pb-Einzelwerte um die Mittelwerte auf (V = 54,2 % bzw. 39,0 %). Selbst bei Tieren aus gleichen Beständen oder dem gleichen Ort waren sie kaum geringer. Die Variationskoeffizienten schwankten bei Lebern innerhalb der Einzelkollektive zwischen 20 und 46 %, bei Nieren zwischen 18,5 und 53,5 %.

Dennoch bestand zwischen der Pb-Konzentration in Leber und Nieren des Einzeltieres, innerhalb der Kollektive und der Gesamtheit der untersuchten Tiere ein hochsignifikanter Zusammenhang ($\alpha = 0{,}001$). Rinder mit hohen Leber-Pb-Werten weisen demnach auch hohe Pb-Konzentrationen in den Nieren auf.

Eine statistisch gesicherte Abhängigkeit der Pb-Konzentrationen in Nieren und Lebern vom Alter der Tiere besteht, wie ein Blick auf die Korrelationskoeffizienten in Tabelle 2 und 3 beweist offenbar nicht. Deshalb kann auch die Frage, ob die Pb-Konzentrationen in Organen von Rindern ähnlich wie beim Menschen mit steigendem Alter zunehmen (10) oder der Einbau des Pb bereits nach einer bestimmten Zeit im wesentlichen abgeschlossen ist (4) anhand des vorliegenden Untersuchungsmaterials nicht schlüssig beantwortet werden. BARRY (4) beobachtete bei Menschen in Weichgeweben nach dem ersten Lebensjahrzehnt kaum mehr eine Pb-Zunahme.

Auch ein jahreszeitlicher Einfluß auf die Pb-Konzentrationen von Leber und Nieren war statistisch nicht absicherbar. Allerdings ergab der t-Test beim Vergleich der Pb-Gehalte von Lebern und Nieren 1972 und 1973 geschlachteter Tiere nur 1972 für Lebern signifikant höhere Pb-Werte ($t = 1,89$; $n = 77$; $\alpha = 5$ %). Möglicherweise begünstigten die 1972 nur geringen Niederschlagsmengen diesen Umstand.

Die weitere Aufschlüsselung des Untersuchungsmaterials nach Rasse, Geschlecht, Herkunft, Haltung und Fütterung lieferte bis jetzt noch keine zusätzlichen Anhaltspunkte für eine Erklärung der gefundenen großen Schwankungsbreiten im Pb-Gehalt von Lebern und Nieren.

Die Ursache dafür dürfte primär individuell bedingt sein und muß vermutlich in Unterschieden bei der Absorption, Verteilung und Ausscheidung des Pb in verschiedenen Tierkörpern gesucht werden. Sie würden auch erklären, warum selbst bei gleichalten, gleichgeschlechtlichen Tieren eines Bestandes ähnlich große Schwankungen gefunden wurden wie innerhalb der Tierkollektive.

Ein Blick auf Tabelle 4 läßt erkennen, daß stärker Pb-exponierte Rinder in Leber und Nieren zumeist erheblich höhere, in Fleisch dagegen nur geringfügiger erhöhte Pb-Konzentrationen aufweisen als die von uns in weniger stark umweltbelasteten Arealen untersuchten Rinder. Wenn sie mit den Symtomen einer Pb-Vergiftung notgeschlachtet worden waren, enthielten ihre Lebern und Nieren Pb-Konzentrationen, die den Verdacht einer lebensbedrohlichen Pb-Intoxikation rechtfertigten. Die Zunahme des Pb in den Fleischproben war auch bei diesen Tieren nur gering. Diese Befunde decken sich mit einer Mitteilung HÖGGERS (19), der bei drei 36 Tage mit Heu von einem Autobahnmittelstreifen (99 mg Pb/kg TS) gefütterten Kühen in Lebern und Nieren über eine starke, in der Muskulatur dagegen nur schwache Zunahme der Pb-Konzentrationen berichtete. Auch unseren Untersuchungen zufolge, bedarf es für eine erhebliche Erhöhung des Pb-Gehaltes in Leber und Nieren von Rindern des Zusammentreffens einer Reihe die Akkumulierung des Pb in Futter und Tieren optimal begünstigender Faktoren. Bei Rindern aus autobahnnahen Betrieben konnte bis jetzt erst bei einer Kuh in Fleisch ein signifikanter Anstieg der Pb-Konzentration beobachtet werden. Das Tier stammte aus einem 10m tiefer, unmittelbar neben der Autobahn in Richtung der Hauptwinddrift gelegenen Betrieb, wo zum Tränken der Rinder Wasser aus einem Tümpel verwendet wird, der Sickerwasser und auch von der Autobahn herabrinnendes Regenwasser aufnimmt. Daß Rinder aus autobahnnahen Betrieben bisher in Nieren und Lebern keine stärker erhöhten Pb-Konzentrationen aufwiesen, dürfte mit darauf zurückzuführen sein, daß die Tierbesitzer entweder von sich aus auf die Verfütterung von unmittelbar neben der Autobahn gewachsenem Futter verzichten oder den Tieren in erheblichem Umfang weniger stark Pb-kontaminierte Futtermittel zufüttern.

Die in den eigenen Untersuchungen bei Fleisch, Lebern und Nieren von weniger und stärker Pb-exponierten Rindern ermittelten Pb-Konzentrationen entsprechen im wesentlichen den in der Literatur mitgeteilten Werten (Tabelle 1 und 4). Allerdings ist ein Vergleich nur bedingt möglich, da es zumeist an detaillierten Angaben zur Probenahme fehlt.

Der durchschnittliche Pb-Gehalt der Nahrung beträgt in England 0,13 ppm (44; 45). Vergleicht man damit die Pb-Werte in Fleisch, Lebern und Nieren der von uns untersuchten, weniger stark Pb-exponierten Rinder , so zeigt sich, daß Fleisch relativ geringe, Lebern durchschnittliche und Nieren über dem Durchschnitt gelegene Pb-Konzentrationen aufweisen. Auch Fleisch von stärker Pb-exponierten oder sogar mit Symptomen einer Pb-Vergiftung notgeschlachteten Rindern enthielt fast stets Pb-Konzentrationen unter 0,13 ppm/Fg.

Fleisch zählt demnach zu den bleiarmen, die Nieren zu den bleireicheren Lebensmitteln. Lebern enthalten etwa Durch-

schnittswerte.
Der Anteil des Fleisches am Gesamt-Pb-Gehalt der Nahrung kann daher als gering veranschlagt werden. Das gleiche trifft trotz höherer Pb-Konzentrationen auch für Lebern und Nieren zu, wenn man deren geringen Beitrag an der Gesamtnahrung in Rechnung stellt.
Allerdings sollte hier auf bestimmte Kontrollmaßnahmen nicht verzichtet werden, da Nieren auch bei stärker Pb-exponierten Rindern bereits beachtliche Pb-Konzentrationen enthalten.
Legt man den im Entwurf der "VO über Umweltkontaminanten" der BRD für Innereien diskutierten zulässigen Höchstwert von 0,3 ppm Pb/Fg zugrunde, hätten 55 % der von uns untersuchten Nieren und 1,5 % der Lebern Pb-Konzentrationen über diesem Toleranzwert besessen.
Auch bei Zugrundelegung einer Toleranz von 0,5 ppm Pb/Fg überschreiten immer noch 10,8 % der untersuchten Nieren diesen Wert.
Es wird deshalb vorgeschlagen, für Nieren eigene Pb-Toleranzwerte zu erstellen.

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